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Data User's Guide to the United States Environmental Protection Agency's Long-term Monitoring Project:

Quality Assurance Plan and Data Dictionary

Front cover: Carolyn Peduzzi and Jim Kellogg, of the Vermont Department of Environmental Conservation, sampling Pigeon Pond, Vermont. Photo by John Slade.

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Quality Assurance Plan and Data Dictionary

Part I: Quality Assurance Plan for the Long-Term Monitoring Project

By

Marilyn Morrison
ManTech Environmental Technology, Inc.
c/o U.S. EPA Environmental Research Laboratory
200 S.W. 35th Street
Corvallis, OR 97333

Part II: Long-Term Monitoring Project Data Dictionary

By

Avis D. Newell and Randy Hjort
ManTech Environmental Technology, Inc.
c/o U.S. EPA Environmental Research Laboratory
200 S.W. 35th Street
Corvallis, OR 97333

Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Corvallis, OR 97333

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PART I:
QUALITY ASSURANCE PLAN
FOR THE
LONG-TERM MONITORING PROJECT

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By

Marilyn Morrison
ManTech Environmental Technology, Inc.
U.S. EPA Environmental Research Laboratory
200 SW 35th Street
Corvallis, Oregon 97333

CONCURRENCES:

Name: Jesse Ford
Title: LTM Technical Director
Signature: Jesse Ford Date: 08 Feb 90

Name: Dixon Landers
Title: EPA Project Officer
Signature: Dixon Landers Date: 07 Feb 90

Name: Robert Lackey
Title: EPA QA Officer
Signature: Robert T. Lackey Date: 2/12/90

LTM Cooperators:

Name: Charles Driscoll
LTM Region: Adirondacks
Affiliation: Syracuse University
Signature: Charles Driscoll Date: 12 November 1989

Name: Peter Murdoch
LTM Region: Catskills
Affiliation: U.S. Geological Survey, WRD, Albany, NY
Signature: Peter Murdoch Date: 11/22/89

Name: John Turk
LTM Region: Colorado
Affiliation: U.S. Geological Survey, Lakewood, CO
Signature: John Turk Date: 11/20/89

Name: J. Steve Kahl
LTM Region: Maine
Affiliation: University of Maine
Signature: J. Steve Kahl Date: 11/13/89

Name: Patrick Brezonik
LTM Region: Upper Midwest Region
Affiliation: University of Minnesota
Signature: Patrick L. Brezonik Date: 2/12/90

Name: Katherine Webster

LTM Region: Upper Midwest Region

Affiliation: Wisconsin Department of Natural Resources

Signature: Katherine E. Webster Date: 21 November 89

Name: Jim Kellogg

LTM Region: Vermont

Affiliation: Vermont Department of Environmental Conservation

Signature: James H. Kellogg Date: 11/9/89

Name: Doug Burnham

LTM Region: Vermont

Affiliation: Vermont Department of Environmental Conservation

Signature: Douglas G. Burnham Date: 11/9/89

SECTION 1
PROJECT DESCRIPTION, ORGANIZATION, AND QUALITY ASSURANCE OBJECTIVES

1.1 PROJECT DESCRIPTION

The U.S. Environmental Protection Agency (EPA) Long-Term Monitoring (LTM) Project for lakes and streams was initiated in 1983 within the National Acid Precipitation Assessment Program (NAPAP) Task Group E organizational framework. The objectives were to detect and measure trends in the chemistry of low acid neutralizing capacity (ANC) surface waters over gradients of H^+ and SO_4^{2-} deposition in different geographic regions. The LTM Project consists of cooperators affiliated with several federal agencies and universities in different regions. The EPA Environmental Research Laboratory in Corvallis, Oregon (ERL-C), manages the LTM Project and coordinates the LTM cooperators.

An ad hoc committee, with representation from the EPA, the U.S. Geological Survey (USGS), the Tennessee Valley Authority (TVA), the U.S. Forest Service (USFS), the U.S. Fish and Wildlife Service (USFWS), and the U.S. National Park Service (USNPS), developed a draft sampling and analysis protocol in 1983 to standardize monitoring efforts among the Task Group E agencies. In 1984, the EPA initiated the National Surface Water Survey (NSWS). The methods manual developed for the NSWS (Hillman et al., 1986) was used, together with the 1983 Task Group E sampling and analysis protocol draft, to produce the working protocol for sampling, sample analysis, and quality assurance/quality control (QA/QC) for the EPA LTM Project (Appendix A). The objective was to align the long-term monitoring methodology with that of NSWS, without undue disruption of existing monitoring procedures. This protocol, completed in May 1985, has served as the standard protocol for the LTM Project. Note that sampling for LTM began in 1983, although the standardized protocol was not completed until 1985. This document, the LTM QA Plan, is the latest revision of the original protocols.

The LTM Project originally was to be replaced in 1988 by the Temporally Integrated Monitoring of Ecosystems (TIME) Project, the long-term monitoring phase of NSWS. Implementation of the TIME Project has been delayed, however, due to changing priorities within the EPA. Sampling in several of the LTM regions has been extended because of this delay. A primary justification for continuing the LTM Project was to maximize the length of record of the LTM data set so it could be analyzed for trend information for the 1990 Assessment Report to NAPAP.

A report analyzing the data from the LTM Project, *Analysis of Data from Long-Term Monitoring of Lakes* (Newell et al., 1987) was completed in 1987; it included LTM data collected through 1985. One of the summary comments in the report noted the lack of adequate quality assurance data for effectively describing the quality of the LTM data. It was suggested that the number of duplicate samples be increased to improve the confidence of precision estimates and that more stable performance audit samples be provided so interlaboratory comparisons could be made. This revision of the QA protocols incorporates those suggestions, so that the quality of the data collected in the coming years can be adequately described.

1.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

The current LTM Project consists of cooperators located in Maine, Vermont, the Adirondacks (New York), the Upper Midwest (Minnesota, Wisconsin, and Michigan), the Rocky Mountains (Colorado), and the Catskills (New York). The target resource includes lakes in all regions except the Catskills, where streams are monitored. Table 1-1 lists the current LTM cooperators, their locations, the number of sites, the sampling schedules, and the dates when monitoring began at those locations. Each cooperator is responsible for sampling, analysis, QA/QC procedures, data validation, and data reporting to the U.S. EPA Environmental Research Laboratory in Corvallis, Oregon. Sections 4 through 9 contain information specific to each LTM region. ERL-Corvallis is responsible for coordination among the LTM projects, data management of the combined LTM data set, coordination of the performance evaluation program, and final reporting of the LTM data. The QA procedures described in this document make up the minimum requirements that each cooperator must follow.

1.3 QUALITY ASSURANCE OBJECTIVES

1.3.1 Required Measurements

A set of required measurements was specified for the LTM Project that would provide sufficient characterization of stream or lake water quality to assess the sensitivity and change related to acidification; these measurements are:

- pH (field or field laboratory, and air-equilibrated)
- Acid neutralizing capacity (ANC)
- Specific conductance
- Temperature

TABLE 1-1. EPA LONG-TERM MONITORING PROJECTS

Location	Cooperators	Affiliation	Number of sites[a]	Start of Sampling	Sampling Schedule	Comments
Adirondacks, (New York)	Charles Driscoll	Syracuse U.	16 lakes	Spring 1985	Monthly	Previous data, sampled monthly, from 1982-1984[b].
Vermont	Wallace McLean, Doug Burnham	Vermont Agency of Environmental Conservation	24 lakes	Winter 1981	Seasonal	Sampling and analytical changes (SO_4^{2-}) occurred in spring 1985.
Maine	Terry Haines, Jeffrey S. Kahl	USFWS; U. of Maine	5 lakes	Spring 1982	Spring, summer, fall	
Upper Midwest	Patrick Brezonik	U. of Minnesota; Wisconsin Dept. of Natural Resources			Spring, summer, fall	Previous data, sampled sporadically on a seasonal basis, from 1978 to 1983[c].
(Minnesota)			4 lakes	Fall 1983		
(Wisconsin)			12 lakes	Fall 1983		
(Michigan)			11 lakes	Fall 1983		
Rocky Mountains, (Colorado)	John Turk	USGS, Denver	10 lakes	Summer 1985	Monthly in summer	
Catskills (New York)	Pete Murdoch	USGS, Albany	4 streams	Fall 1983	9 times per year	Sampling is flow directed

[a] Number of sites funded by U.S. EPA. in 1989.

[b] Two years of additional data collected for most of these lakes between 1982 and 1985 by Syracuse University were funded by the Electric Power Research Institute during the Regional Integrated Lake Watershed Acidification Study (Driscoll, pers. comm).

[c] Data collected by the University of Minnesota-Duluth through a cooperative agreement with the Environmental Research Laboratory, Duluth, are available for most of these lakes for the period 1978-1982 (Glass, pers. comm). The sampling schedule for these lakes was variable, ranging from twice a year to seasonally, and included multiple samples per lake.

- Secchi disc transparency (lakes)
- True color
- Major cations (Ca, Mg, Na, K)
- Major anions (SO_4^{2-}, NO_3^-, Cl^-)
- Total filtered aluminum

Additional measurements, including titrated acidity, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), F^-, Fe, Mn, NH_4^+, SiO_2, and total P, were made by NSWS; some of these analyses, while not required, are also being performed by some cooperators in the monitoring program.

1.3.2 Quality Assurance (QA) Objectives

Table 1-2 lists the required detection limits and QA objectives for intralaboratory precision and accuracy. In addition, accuracy and bias are assessed through the Long-Range Transport of Airborne Pollutants (LRTAP) Interlaboratory Comparability Studies. In these studies, a flag is assigned to an audit sample result if the result exceeds the acceptable limit for difference from the median value. Acceptable limits for each variable were established by the LRTAP program. Any flags assigned are investigated. Bias for each variable is assessed by the LRTAP study with an interlaboratory ranking procedure. The objective for bias identified by LRTAP results is to avoid having a bias class greater than "slightly low" or "slightly high." If a variable has a bias identified for two consecutive LRTAP studies, the cause of the bias must be determined. Section 3.2 describes the specific procedures used for assessing precision, accuracy, and bias, and Section 3.2.6 describes the LRTAP Comparability Studies.

Specific objectives for LTM cooperators include comparability, completeness, and representativeness. For comparability, data collected by each LTM cooperator should be comparable from year to year and comparable with data from other laboratories performing acid precipitation research. Comparability will be assessed with the LRTAP studies, by comparing each laboratory's performance index over time. The objective is to have similar performance indices from year to year. For completeness, each cooperator should collect and analyze 90% of the samples initially planned for collection. Finally, for representativeness, samples should be representative of trends over time.

TABLE 1-2. QUALITY ASSURANCE OBJECTIVES: REQUIRED ANALYTICAL DETECTION LIMITS, WITHIN-LABORATORY RELATIVE PRECISION, AND ACCURACY OBJECTIVES

Variable	Reporting Units	Required Detection Limit	Intralab Relative Precision (%)[a]	Accuracy (%)[b]
Required measurements				
pH, field or field lab	pH units	--	± 0.1 pH unit	--
pH, air equilibrated	pH units	--	± 0.05 pH unit	--
ANC	µeq/L	--	± 5 µeq/L (if ANC≤30) 10% (if ANC>30)	
Conductivity	µS/cm	--[c]	± 2 µS/cm (if cond. ≤25) 5% (if cond. >25)	5
Color	Pt-Co units	0	± 5 Pt-Co units	--
SO_4^{2-}	µeq/L	1.0	5	10
NO_3^-	µeq/L	0.1	± 2 µeq/L (if NO_3^-<15) 10% (if NO_3^-≥15)	10
Cl^-	µeq/L	0.3	5	10
Ca	µeq/L	0.5	5	10
Mg	µeq/L	0.8	5	10
Na	µeq/L	0.4	5	10
K	µeq/L	0.3	5	10
Al, total dissolved	µg/L	5	20 (if Al≤50 µg/L) 10 (if Al>50 µg/L)	20 (if Al≤50 µg/L) 10 (if Al>50 µg/L)
Additional Measurements:				
Acidity	µeq/L	5	10	10
DIC	mg/L	0.05	10	10
DOC	mg/L	0.1	10 (if DOC≤5 mg/L) 5 (if DOC>5 mg/L)	10
F^-	µeq/L	0.3	5	10
Fe	mg/L	0.01	10	10
Mn	mg/L	0.01	10	10
NH_4^+	µeq/L	0.6	5	10
SiO_2	mg/L	0.05	5	10
P, Total	µg/L	2	20 (if P≤10 µg/L) 10 (if P>10 µg/L)	20 (if P≤10 µg/L) 10 (if P>10 µg/L)

[a] Expressed as percent relative standard deviation (standard deviation divided by the mean) when concentrations measure at least 10 times above instrumental detection limits (unless concentration range is noted), or, if ± units appear, as plus or minus the specified number of units.

[b] Expressed as percent difference from a reference value.

[c] Blank must be < 2.0 µS/cm.

SECTION 2
SAMPLING AND ANALYTICAL PROCEDURES

2.1 SAMPLE CONTAINERS: CLEANING AND CONDUCTIVITY CHECKS

Sample containers for required variables should be composed of high-density linear polyethylene. Containers to be used for pH, ANC, and anion analyses shall be rinsed three times with deionized water, filled with deionized water, and allowed to stand for at least 48 hours, then emptied and rinsed with sample water in the field.

Soak the sample containers for cations and metals in 10% HCl for 12 hours, then rinse them 6 times with deionized water. Next, fill the containers with deionized water and allow them to stand for 48 hours, then empty and refill them with deionized water until they are used for collecting samples. The containers should not be allowed to dry between acid washing and sample collection.

At least 50% of the cleaned (selected randomly) containers must be given a conductivity check. Measure the conductivity of the deionized water in the container after the 48-hour period. If the conductivity is > 2.0 μS/cm, rerinse all the containers in that batch. Record in the laboratory notebook the highest conductivity value for each batch. Since container contamination is random and is most likely to be caused by incomplete rinsing after acid washing, increasing the number of conductivity checks will give better assurance that each container has been thoroughly cleaned and rinsed prior to being used to collect samples.

2.2 SAMPLE COLLECTION

2.2.1 Lakes

Lakes should be sampled near their deepest points, at least 20 m from shore if possible. If the water column is not thermally stratified, that is, if the temperature difference between the top and bottom of the water column is < 4°C (Drousé et al., 1985), one sample should be collected approximately one-half meter beneath the water surface. If the water body is stratified, an epilimnetic sample should be collected approximately one-half meter beneath the water surface and a hypolimnetic sample collected one or two meters above the bottom. These two samples are to be analyzed separately, and not mixed. A plastic Van Dorn type sampling device should

be used to obtain samples at depth; do not use a metal sampler. Samples should be collected from the sampling device in plastic bottles that have been prepared as described in Section 2.1. See Section 3.1.1 for guidance in collecting duplicate samples.

2.2.2 Streams

Samples should be obtained by hand as near mid-stream as possible, using a properly cleaned and rinsed plastic container. Keep hands away from mouth of container. See Section 3.1.1 for guidance in collecting duplicate samples.

2.2.3 Field Laboratory Notebook

Carefully record in field notes or a sampling log any observed conditions that might affect analysis or interpretation of samples, for example, weather conditions or recent shore activities. Key project personnel who are responsible for sample integrity must be identified in the notebook. Guidelines for laboratory notebooks are given in Appendix B.

2.3 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

2.3.1 Labels

Labels on all containers should include sufficient information to permit tracing the sample back to the point and time of sample collection: lake name or ID, collection date, aliquot name, and sample preservation.

2.3.2 Filtration and Preservation Protocol for Anion Analyses (SO_4^{2-}, NO_3^-, Cl^-)

Filter aliquots for anion analyses as soon as possible after sample collection. Rinse a membrane filter of 0.4-µm pore size (e.g., polycarbonate or cellulose-based), with approximately 100 mL deionized water and two 20-mL aliquots of sample. Rinse the sample container with the two filtered sample water rinses, then discard each rinse. Filter the required amount of sample (60 to 100 mL) into the container. If more than one filter is used for a sample, rinse each filter before use. Ice or refrigerate the filtered sample.

2.3.3 Filtration and Preservation Protocol for Cation Analyses (Ca, Mg, Na, K, and Al)

Filter aliquots for cation analyses as soon as possible after sample collection. Rinse the filters as described for anions: rinse a membrane filter of 0.4-μm pore size (e.g., polycarbonate or cellulose-based) with approximately 100 mL of deionized water and two 20-mL aliquots of sample. Rinse the acid washed sample container with the two filtered sample water rinses, then discard each rinse. Filter the required amount of sample (60 to 100 mL) into the container, and add ultra-pure or an equivalent nitric acid to acidify the sample to < pH 2.0. If more than one filter is used for a sample, rinse each filter before use. Ice or refrigerate the filtered sample.

2.3.4 True Color and DOC

Aliquots for true color are either centrifuged or filtered. Aliquots for DOC are filtered. All cooperators should continue to follow the protocols for color and DOC that they have followed in the past; these protocols are listed in Sections 4 through 9.

2.3.5 pH, ANC, and Specific Conductance

Aliquots for pH, alkalinity, and specific conductance are not filtered or acidified.

2.3.6 Sample Preservation and Holding Times

Table 2-1 lists the preservation and storage requirements for each of the required variables, and the maximum allowable holding times. The holding time is the time between sample collection and sample analysis. Records must be kept of the holding time for each variable for each sample. A list of each sample by variable with any holding time exceeding those in Table 2-1 must be included when data are reported to ERL-Corvallis. Decisions to use the data for trend detection are not made until all data for that sample (e.g., ion balances, conductivity checks) have been evaluated.

2.4 ANALYTICAL METHODS

Table 2-2 lists the analytical methods for each required measurement.

TABLE 2-1. SAMPLE PRESERVATION AND HOLDING TIMES FOR REQUIRED MEASUREMENTS

Variable	Sample Preservation	Maximum Holding Time[a]
pH, field	closed container	measured on site
pH, air equilibrated	store at 4°C	7 days
ANC	store at 4°C	14 days
Color	filtered or centrifuged, store at 4°C	48 hours
Conductivity	store at 4°C	14 days
SO_4^{2-}	filter thru 0.4 µm, store at 4°C	28 days
Cl^-	filter thru 0.4 µm, store at 4°C	28 days
NO_3^-	filter thru 0.4 µm, store at 4°C	7 days
Ca	filter thru 0.4 µm, store at 4°C, acidify with HNO_3 to < pH 2.0.	6 months
Mg	filter thru 0.4 µm, store at 4°C, acidify with HNO_3 to < pH 2.0.	6 months
Na	filter thru 0.4 µm, store at 4°C, acidify with HNO_3 to < pH 2.0.	6 months
K	filter thru 0.4 µm, store at 4°C, acidify with HNO_3 to < pH 2.0.	6 months
Al	filter thru 0.4 µm, store at 4°C, acidify with HNO_3 to < pH 2.0.	6 months

[a] Holding times from Drousé et al., 1985.

TABLE 2-2. ANALYTICAL METHODS FOR REQUIRED MEASUREMENTS

Variable	Method	Reference
pH, field	Electrode	Section 2.5.1
pH, air equilibrated	Electrode, aeration with 300 ppm CO_2	Hillman et al., 1986
ANC	Titration with Gran plot	Gran, 1950, 1952; Hillman et al., 1986
Conductivity	Conductivity cell	U.S. EPA, 1979
True Color	Comparison of centrifuged or filtered samples with platinum-cobalt color standards	U.S. EPA, 1979
SO_4^{2-}, Cl^-, NO_3^-	Ion chromatography	Hillman et al., 1986; O'Dell et al., 1984
Ca, Mg	Atomic absorption spectrophotometry (AAS), add La or use N_2O flame	U.S. EPA, 1979
Na, K	AAS	U.S. EPA, 1979
Al, total	Graphite furnace AAS	U.S. EPA, 1979; Hillman et al., 1986

2.5 CALIBRATION PROCEDURES

2.5.1 pH

pH should be measured to the hundredths unit using a high-quality pH meter with an expanded or digital scale. An electrode designed for low ionic strength solutions, such as the Orion Ross Combination Model 81-02, should be used. The electrode should be calibrated with pH 4.0 and 7.0 buffer solutions and then checked with a dilute acid solution. The dilute acid solution can be made by diluting the acid used for ANC titrations 1:1000. For example, a 1:1000 dilution of 0.02 N H_2SO_4 or HCl will produce a solution with a theoretical pH of 4.70. Rinse the electrode copiously with sample or deionized water before immersing in the sample. A duplicate should be measured after every 10 samples, and the dilute acid solution should be measured at the completion of a sample batch. Two types of pH measurements are to be performed, one on an unagitated sample in the field or field laboratory, and another on an air-equilibrated sample in the laboratory.

Measure field pH as soon after collection as possible. The electrode should remain in the unagitated sample until there is no discernible drift in the pH reading, but no longer than 15 minutes.

Air-equilibrated pH is measured in the laboratory for intercomparison of the pH values obtained by various participating investigators. Equilibration is achieved by bubbling samples with standard air containing 300 ppm CO_2 for 20 minutes while stirring on a magnetic stirrer. A fritted plastic diffuser is used for dispersal of air in the sample. Measure pH immediately following equilibration. A duplicate should be measured after every 10 samples, and the dilute acid solution should be measured at the completion of a sample batch.

2.5.2 Atomic Absorption Spectrophotometer (AAS): Ca, Mg, Na, K, and Al

Calibrate the AAS with standards made from American Chemical Society (ACS) reagent grade chemicals or from atomic absorption reference standards. At least three standards spanning the concentration range of the samples must be used for calibration. Measure QC samples after the instrument has been calibrated and before the samples are analyzed, and after every 10 samples. At a minimum, the QC samples should be analyzed three times in each batch: at the beginning, in the middle, and at the end of the batch. A batch is the set of samples

analyzed with the same calibration curve. QC samples are prepared from a source independent of the calibration standards. Ideally, there should be two QC samples at two different concentrations in the working range; if only one QC sample is used, one or more of the calibration standards should also be rerun once every 10 samples.

QC samples are used by the analyst to keep the analytical instrument in control. The acceptable range of measured QC sample values for Ca, Mg, Na, and K is a 5% difference from the theoretical value; the range for Al is a 10% difference from the theoretical value. If the QC sample is out of this range, the source of the problem must be determined and the situation corrected before more samples are analyzed. The set of samples analyzed after the last acceptable QC value was obtained are reanalyzed.

2.5.3 Ion Chromatograph (IC): SO_4^{2-}, Cl^-, and NO_3^-

Calibrate the IC with standards made from ACS reagent grade chemicals or from IC reference standards. Three to seven standards spanning the concentration range of the samples must be used for calibration. The same QC sample procedure described for the AAS in Section 2.5.2 should be used for the IC. Measure QC samples or standards at least every 10 samples to check the calibration. The acceptable range of measured QC values for SO_4^{2-} and Cl^- is a 5% difference from the theoretical value; for NO_3^-, the range is a 10% difference from the theoretical value.

2.5.4 Specific Conductance

Check the calibration of the conductivity meter daily with a standard KCl solution with a conductance of < 50 µS/cm and calibrate if necessary (if the meter can be calibrated), or recalculate the cell constant. Before measuring the first sample, measure the conductance of a QC standard. The standard should have a theoretical or certified conductance in the conductivity range of the samples. If the measured conductivity is not within $\pm$ 5% of the certified value, then restandardize the meter and cell and repeat the measurement. Remeasure the conductance of the QC standard at least once every 20 samples. One sample per batch must be measured in duplicate.

SECTION 3
QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

Table 3-1 contains a summary of quality assurance and quality control (QA/QC) samples for the LTM Project.

3.1 QUALITY CONTROL PROCEDURES

3.1.1 Field Duplicates

Collect field duplicates as collocated samples, that is, one after another at the same point in the lake or stream. After collecting the samples into separate containers, filter and analyze the field duplicates as two discrete samples. Collect a field duplicate once for every 10 lakes sampled, with a minimum of 2 pairs of field duplicates during each sampling round. Table 3-2 lists the number of field duplicates to be collected by each project. Field duplicates are used to estimate the precision of the sampling process, including analytical precision.

3.1.2 Field Blanks

Collect a field blank by bringing deionized water (with conductivity < 2.0 µS/cm) to the field site and transferring the deionized water into containers normally used to collect the sample from the Van Dorn sampler. From that point on, process the blank as if it were a regular sample; blank aliquots are to be (1) unfiltered for pH, ANC, and conductivity, (2) filtered for anions, (3) filtered and acidified for cations, and (4) filtered for DOC and true color. Field blanks should be collected once for every 10 sites sampled, or a minimum of 2 per sampling round. Analysis of the blanks serves as a check on the presence of contamination from the sampling process. Table 3-3 provides guidelines for determination of contamination. Contamination should be assumed if analysis of a field blank yields values equal to or higher than those listed in Table 3-3.

3.1.3 Filter Blanks

Prepare filter blanks by filtering deionized water (with conductivity < 2.0 µS/cm) into properly cleaned anion and cation containers. Preserve the filter blanks in the same manner as for regular samples. A set of filter blanks (one for anions and one for cations) should be collected once for every 10 lakes sampled. Filter blanks are archived until after the field blanks and regular

TABLE 3-1. SUMMARY OF QA/QC SAMPLES FOR LTM

Sample Type	Frequency	Purpose
Field Duplicates	Minimum of 2 per sampling round; or 1 per 10 sites	Estimate sampling and analytical precision
Lab Duplicates	Minimum of 2 per analytical batch	Estimate analytical precision
Field Blanks	Minimum of 2 per sampling round; or 1 per 10 sites	Detect contamination from sample processing, including filtration
Filter Blanks	1 set (1 each for cations, anions, DOC) per 10 sites; only analyzed if problem with field blanks	Detect contamination from filtering process
QC Sample	Measured 3 times per analytical batch	Check instrument performance and calibration; estimate analytical precision and accuracy
Spiked Samples	1 per analytical batch (optional[a])	Estimate instrument performance, % recovery, and matrix effects
Certified Reference Material	1 per analytical batch (optional[a])	Estimate accuracy
Performance Evaluation Samples: LRTAP Round Robin and synthetic AI audits	3 times per year	Detect lab bias, estimate accuracy, evaluate lab performance over time

[a] Note: For estimates of accuracy, either calibration QC samples, spiked samples, or certified reference material must be used.

TABLE 3-2. MINIMUM NUMBER OF DUPLICATES PER SAMPLING INTERVAL

Region	Number of Duplicates	Sampling Intervals
Upper Midwest	3	spring, summer, fall
Colorado	2	monthly for 3 months
Adirondacks	2	monthly
Maine	2	spring, summer, fall
Vermont	2	spring, summer, fall, winter
Catskills	2	9 times per year

TABLE 3-3. GUIDELINES FOR DETERMINATION OF CONTAMINATION FROM ANALYSIS OF BLANK SAMPLES

Variable	µeq/L[a]	mg/L[a]
ANC	10	
pH	--	
Conductivity	4 µS/cm	
Ca	1.0	0.02
K	0.6	0.02
Mg	2.0	0.02
Na	0.8	0.02
Cl^-	1.0	0.02
NO_3^-	0.2	0.01
SO_4^{2-}	2.0	0.1
Color	0 Pt-Co Units	
DOC		0.2
Al		0.01 (10 µg/L)
F^-	0.6	0.01
P, total		0.004 (4 µg/L)
SiO_2		0.1

[a] These values are obtained by approximately doubling the required detection limit values listed in Table 1-2. They are meant as guidelines to the analyst, to expedite the detection of contamination and analytical problems. Contamination is assumed if analysis of a field blank yields values equal to or higher than the values listed here. For most lakes, these values are well below the expected values for most variables, although nitrate and phosphorus values are often at or below these values and the detection limits. Blank values for ANC and pH are difficult to quantify, yet blanks can still give information about contamination of these variables as well. Keep in mind that these values are presented as guidelines, and use common sense and prior knowledge about the systems in question to help determine the quality of data at hand.

samples have been analyzed, the data have been analyzed, and the data have been evaluated for suspected problems. The filter blanks need to be analyzed only if a contamination problem is indicated by the field blanks or the analysis of the lake data.

3.1.4 Quality Control (QC) Samples

QC samples are used to check the calibration of analytical instruments. QC samples are analyzed a minimum of three times in each analytical batch. A complete description of the use of QC samples is given in Section 2.5.2, Calibration Procedures for AAS.

3.1.5 Laboratory Duplicates

Laboratory duplicates are samples split into separate containers after filtration (if appropriate) but prior to analysis, and analyzed as separate samples within the same batch. There should be a laboratory duplicate for every 10 samples, with a minimum of 2 pairs per batch. Laboratory duplicates are used to estimate within-batch analytical precision.

3.1.6 Spiked Samples

The use of spiked samples is optional, but if they are used to estimate within-batch accuracy, a spiked sample should be prepared for each batch for each analyte being measured. Prepare a spiked sample by adding a known quantity of analyte to an aliquot of a sample, then analyzing the analyte in the spiked and unspiked aliquots. A percent recovery can then be calculated (see equation 3 in Section 3.2.7) and used as an estimate of accuracy. The spike concentration should be at least 10 times the detection limit for the analyte, and should keep the measured value of the spiked sample within the linear range of the analytical instrument. The volume of the spike added should be negligible.

3.1.7 Analytical Detection Limit

Measurement of analytical detection limit was not required in the 1985 Working Protocol for Sampling, Sample Analysis, and QA/QC for LTM (Appendix A). However, measurement of the analytical detection limit on a regular basis is necessary for monitoring programs in order to provide regular assessment of instrument performance, as well as a quantifiable concentration that will indicate when a measured value is above zero and is in fact detectable by the analytical

instrument. The analytical detection limit can be defined as three times the standard deviation of a low-level check standard (Taylor, 1987). The concentration of the low-level check standard should be three to five times the required analytical detection limit as listed in Table 1-2. The low-level check standard should be used to monitor batch-to-batch detection limits. In addition, LTM cooperators should measure the actual instrument detection limit quarterly or semiannually by preparing a series of dilutions of the lowest calibration standard. The dilutions are analyzed from the lowest concentration to the highest, with the objective of determining which standard yields a detectable response.

3.1.8 Preparation of Calibration Standards

Analytical balances should be serviced at regular intervals. Weights certified by the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards, class "S" or better, should be used to check the accuracy of the balance prior to each use for preparing standards. If pipets are used in the preparation of standards, the accuracy of each pipet should be verified by weighing the volume of deionized water delivered by the pipet. One mL of deionized water weighs one gram at 25°C.

When new calibration standards are prepared, they must be compared to the standard being replaced and to the other standards for that variable. Never allow standards to be completely used up until a replacement standard has been prepared and compared. Acceptable limits for comparison are within 2% of the theoretical value and of the measured value of the previous standard. The comparison must be recorded. If the 2% limit is not obtained, then a new standard must be prepared and compared with the old standard.

3.2 PROCEDURES FOR ASSESSING PRECISION AND ACCURACY

An estimate of precision and accuracy must be made for each analytical batch of samples, so that the quality of the data can be adequately described. If an analytical batch includes samples other than LTM samples, but similar to LTM samples, duplicates and spikes of the other samples can be used to estimate precision and accuracy for that batch.

3.2.1 Precision

Precision is the degree of mutual agreement characteristic of independent measurements resulting from repeated application of the process under specified conditions (Taylor, 1987). In this program, we estimate (1) analytical and (2) sampling and analysis precision:

- Analytical precision refers to the precision of the analysis performed by analytical laboratory instruments; it is estimated by laboratory duplicates or replicates.
- Sampling and analysis precision refers to the precision of the entire sampling process, from sample collection through analysis; it encompasses analytical precision. It is estimated by field duplicates or replicates.

Both analytical precision and sampling and analysis precision are estimates of intralaboratory precision. Laboratory and field duplicates can be measured within the same analytical batch to estimate within-batch precision, or in different analytical batches to estimate among-batch precision. Among-batch precision includes more sources of error than within-batch precision. QA objectives for precision (Table 1-2) are compared to within-batch analytical precision, although it is desirable for all estimates of precision (i.e., from among-batches and field duplicates) to meet these QA objectives.

Precison is expressed in terms of the coefficient of variation (CV) or percent relative standard deviation (%RSD):

$$CV = \%RSD = s/\bar{X}\ (100) \qquad (1)$$

where: s = standard deviation
$\bar{X}$ = arithmetic mean

3.2.2 Analytical Precision

Analytical precision is determined by analyzing an individual sample in replicate. There are two ways we can measure analytical precision:

- With laboratory duplicates, which are samples split in the laboratory (see Section 3.1.5). A minimum of two pairs of laboratory duplicates per batch should be analyzed for each variable measured. These kinds of duplicates can, in some cases, be blind to the analyst.

- With QC check samples, which are prepared from a source independent of the calibration standards (see Section 2.5.2). QC samples are analyzed after the instrument has been calibrated and before samples are analyzed, and then once after every 10 samples. At a minimum, the QC samples will be analyzed three times in each batch: at the beginning, in the middle, and at the end of the batch. QC samples are used by the analyst to keep the analytical instrument in control; if a QC sample is out of the acceptable range, the problem must be corrected before more samples are analyzed.

3.2.3 Sampling and Analysis Precision

Sampling and analysis precision can be estimated from the analysis of the duplicate samples collected in the field (see Section 3.1.1). One field duplicate is collected for every 10 lakes sampled, with a minimum of at least 2 pairs of field duplicates per batch. The %RSD should be calculated for each pair of duplicates.

3.2.4 Accuracy and Bias

Accuracy is the degree of agreement of a measured value with the true or expected value of the quantity of concern (Taylor, 1987). Accuracy is expressed as the percent difference from the reference value, or as percent recovery if spiked samples have been used. Accuracy can be estimated by measuring: (1) certified reference material or QC check samples, (2) performance evaluation samples, and/or (3) percent recovery on spiked samples. Certified reference materials, QC check samples, and spiked samples will give the analyst an immediate estimate of accuracy, whereas performance evaluation samples will provide an assessment of accuracy and basis for comparison with the other LTM laboratories. Either certified reference materials, QC check samples, or spiked samples should be used with each batch, to estimate accuracy.

Bias is a systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system (Taylor, 1987). The LRTAP Interlaboratory Comparability Studies are used to identify bias in the LTM laboratories. Section 3.2.6 describes the LRTAP Studies.

3.2.5 Certified Reference Material or QC Check Samples

Certified reference material or a QC check sample should be measured in each batch of samples; then the percent difference should be calculated.

$$\% \text{ difference} = \frac{|\text{true value} - \text{measured value}|}{\text{true value}} \times 100 \quad (2)$$

The % difference should be within the QA objectives for accuracy (Table 1-2). If not, corrective action should be taken before samples are analyzed, such as correcting the instrument calibration, or the instrument settings.

Reference materials can be obtained from the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards, or from commercial firms that produce "U.S. EPA Certified" chemical reference materials in cooperation with the EPA. The American Association for Laboratory Accreditation (A2LA) also has a certification program for chemical reference materials that is acceptable to the EPA. Only the terms "U.S. EPA Certified" or "A2LA Certified" indicate certification that has been approved by the EPA. QC check samples can also be prepared from other sources, as long as the source and preparation are different from those used to prepare calibration standards.

3.2.6 Performance Evaluation Samples

Three times a year (approximately April, August, and December) LTM laboratories participate in the Canada Centre for Inland Waters LRTAP (Long Range Transport of Airborne Pollutants) Interlaboratory Comparability Studies (Aspila, 1989). The purpose of the LRTAP studies is to monitor laboratory performance over time. Forty to 50 laboratories participate in each study and analyze 10 natural water samples. A median value for each variable for each sample is determined. Flags (low, very low, extremely low, high, very high, or extremely high) are assigned to variables whose values are outside the acceptable limits for difference from the median value. The acceptable limits for each flag class for each variable are based on results from earlier LRTAP studies.

Laboratory rankings of the results from the 10 samples in each study are used to identify bias for each variable for each laboratory. Bias classes (slightly low, low, slightly high, high) are assigned to a variable based on the procedure described by Youden (1969).

A summary sheet is prepared for each laboratory after a study, indicating the results (flag classes or satisfactory rating, and if ranking indicates a bias) for each variable. If a variable is flagged, first check to see if the value was reported correctly (e.g., that there are no transcription

errors and that unit conversions were made correctly). Results should be discussed with the analyst to identify the source of a flagged result (e.g., calibration errors, dirty equipment, old electrodes, or errors in calibration standards). If a variable is identified as biased in one study, potential sources of bias should be investigated. If a variable is biased two times in a row, special attention should be given to identifying and correcting the source of the bias.

Aluminum is not always included in the LRTAP studies, so occasionally audit samples for analysis of Al will be distributed to the LTM laboratories. The median value of results from all LTM labs will be used to calculate percent difference.

3.2.7 Percent Recovery

Spike an aliquot of a sample with a known amount of analyte (see Section 3.1.6), analyze the spiked and unspiked sample, then calculate the percent recovery. A blank should also be spiked at the same time.

$$\% \text{ Recovery} = [(S - X) / A] \, 100 \qquad (3)$$

where: S = value of sample plus spike
X = value of unspiked sample
A = value of spike added

3.3 DATA VALIDATION AND REPORTING

Once each variable in a sample has been determined, several procedures are used to provide a check on the analyses. These validation checks are completed as soon as possible after analyses are finished, so problems can be detected and samples can be reanalyzed, if necessary, before holding times are exceeded. Validation checks include: (1) cation-anion charge evaluation, (2) specific conductance evaluation, and (3) comparison with previous years' data.

3.3.1 Cation-Anion Charge Evaluation

Theoretically, the sum of anion equivalents equals the sum of cation equivalents in a sample. In practice, this rarely occurs, due to ions that are present but not measured. For each sample, the sums of the measured anion and cation equivalents and the ion ratio are calculated as follows:

$$\Sigma \text{ anions} = [Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}] + [HCO_3^-] + [CO_3^{2-}] \quad (4)$$

$$\Sigma \text{ cations} = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+] + [H^+] \quad (5)$$

$$\text{Ion ratio} = \frac{\Sigma \text{ cations}}{\Sigma \text{ anions}} \quad (6)$$

$$\text{Sum of ions} = \Sigma \text{ anions} + \Sigma \text{ cations} \quad (7)$$

Note: Omission of F^-, CO_3^{2-}, and NH_4^+ will not significantly affect results. ANC plus H^+ (calculated from pH) may be used for HCO_3^-, based on the following equation:

$$ANC = HCO_3^- + 2CO_3^{2-} + OH^- - H^+ \quad (8)$$

when pH < 7.0, CO_3^{2-} and OH^+ are negligible, therefore the equation becomes:

$$ANC = HCO_3^- - H^+; \text{ or } HCO_3^- = ANC + H^+ \quad (9)$$

A percent ion difference can also be calculated instead of an ion ratio to evaluate cation and anion charges:

$$\% \text{ ion difference} = \frac{\Sigma \text{ anions} - \Sigma \text{ cations}}{\Sigma \text{ anions} + \Sigma \text{ cations}} \quad (10)$$

All concentrations are expressed as microequivalents/liter (μeq/L). Table 3-4 lists factors for converting mg/L to μeq/L for each of the variables. Each region has specified the criteria, given as a range of acceptable ion ratios or percent ion differences, that are used to decide if a sample should be reanalyzed. These criteria are given in Sections 4 through 9.

3.3.2 Specific Conductance Evaluation

An estimate of the specific conductance of a sample can be calculated by summing the equivalent conductance values for each measured ion at infinite dilution. The calculated conductance is determined by multiplying the concentration of each ion (in μeq/L) by the appropriate factor (F) in Table 3-5.

TABLE 3-4. FACTORS FOR CONVERTING mg/L TO μeq/L

Ion[a]	Factor (μeq/L per mg/L)
Ca^{2+}	49.9
Cl^-	28.2
CO_3^{2-}	33.3
F^-	52.6
K^+	25.6
Mg^{2+}	82.3
Na^+	43.5
NH_4^+ (as ammonium)	55.4
NH_4^+ (as nitrogen)	71.4
NO_3^- (as nitrogen)	71.4
NO_3^- (as nitrate)	16.1
SO_4^{2-} (as sulfate)	20.8
ANC (as $CaCO_3$)	20.0

[a] Although total forms of Ca, Mg, Na, and K are measured, we assume that all are in ionic form for conversion to microequivalents.

TABLE 3-5. CONDUCTANCE FACTORS (F) OF IONS

Ion[a]	Conductance Factor	Ion[a]	Conductance Factor
Ca^{2+}	59.47	NO_3^-	71.42
Mg^{2+}	53.0	Cl^-	76.31
Na^+	50.08	SO_4^{2-}	80.0
K^+	73.48	HCO_3^-	44.5
H^+	349.65	OH^-	198
NH_4^+	73.50		

[a] H^+ and OH^- calculated as: $H^+ = 10^{-pH} \times 10^6$ µeq/L

$OH^- = 10^{14-pH} \times 10^6$ µeq/L

The calculated conductance for the entire sample is obtained from the relationship

$$\text{Calculated conductance} = \frac{\Sigma\ (F \times \text{Concentration in } \mu eq/L)}{1000} \qquad (11)$$

The percent difference between measured conductance and calculated conductance is given by

$$\%\ \text{conductance difference} = \frac{\text{Calculated} - \text{Measured}}{\text{Measured}} \times 100 \qquad (12)$$

Or, the ratio of calculated to measured conductance can be determined by

$$\text{Conductance ratio} = \frac{\text{Calculated conductance}}{\text{Measured conductance}} \qquad (13)$$

Each region has specified the criteria, given as a range of acceptable percent conductance differences or conductance ratios, that are used to decide if a sample should be reanalyzed. These criteria are given in Sections 4 through 9. The value in error may be difficult to identify, as several numbers are part of the calculated conductance estimate.

3.3.3 Comparison with Previous Years' Data

All newly acquired data should be plotted and compared to historical data from the same lakes or streams within the holding time requirements, if possible, to further assist the detection of any analytical or contamination problems.

3.4 TECHNICAL SYSTEMS AUDITS

On-site technical systems audits are conducted by EPA and technical support QA staff during sampling and analytical activities to ensure that: (1) protocols are being followed properly, (2) each laboratory follows and documents the QA/QC procedures described in this QA plan, (3) the laboratory facilities, personnel, and equipment are capable of continued operations, and (4) problems are being identified and resolved quickly. On-site audits are conducted in each region approximately once every two years.

3.5 QUALITY ASSURANCE REPORTS

Data quality must be indicated whenever data are reported. Data quality is most easily indicated by estimates of precision and accuracy and by the results of blank analyses. Each analytical batch should have an estimate of precision and accuracy, as described in Section 3.2. When raw sample data are reported to ERL-Corvallis, raw data used in estimates of precision and accuracy and in results of blank analyses should also be reported. Summaries of estimates of precision and accuracy for a sampling period can be used when reports on the data are prepared. Precision data can be presented by listing the range of precision values obtained in %RSD by variable for each year or sampling period, noting the number of duplicates, and the number of duplicates that exceeded the QA objectives. Accuracy data can be presented by listing the range of accuracy values in % difference by variable for each year or sampling period, noting the number and type of samples used to determine accuracy, and noting the number of samples that did not meet the QA objectives. Similarly, summaries of blank analyses can be included by listing the range of blank values by variable for each sampling period, the number and concentration of blanks that exceeded the concentration values listed in Table 3-3, and the total number of blank analyses. If the total number of duplicates or blanks is 10 or less, report results from all duplicates or blanks, instead of writing a summary.

SECTION 4
MAINE REGION

This section contains information about specific procedures and methods used in the Maine region through 1989 and was prepared by Jeffrey S. Kahl, Sawyer Environmental Research Center, University of Maine, Orono, Maine, 04469. This information supplements the information in Sections 1 to 3, thus only sections in which region-specific information is required are listed. These sections include project organization and responsibilities (1.2), sample containers (2.1), filtration and preservation protocols (2.3.2 to 2.3.4), analytical methods (2.4), calibration procedures (2.5), procedures for assessing precision and accuracy (3.2.2 to 3.2.4), and data validation criteria (3.3.1 and 3.3.2). The following section numbers and titles in italics correspond to numbers in Sections 1 to 3.

1.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

The Maine LTM program is conducted at the University of Maine, Orono, Maine. The program is operated by Terry A. Haines, U.S. Fish and Wildlife Service, and Jeffrey S. Kahl, Department of Geological Sciences, and Director of the Environmental Chemistry Laboratory (ECL). Terry Haines is responsible for all aspects of the fisheries efforts; Steve Kahl is responsible for field and laboratory activities, QC/QA, data validation, and data reporting in aquatic chemistry. One or two regular staff are utilized for field sampling, and the regular laboratory staff in the ECL analyze the samples.

2.1 SAMPLE CONTAINERS: CLEANING AND CONDUCTIVITY CHECKS

All containers used in the field or laboratory are acid-soaked with HCl for at least one hour, rinsed thoroughly with tapwater, then immediately rinsed four times with deionized water. The containers are then partially refilled with deionized water for storage. The specific conductance of all containers is checked prior to use. If the value is > 2.0 μS/cm, the container is either rejected and put through the entire washing procedure again, or is immediately re-rinsed with deionized water.

2.3 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

2.3.2 Filtration and Preservation Protocol for Anion Analyses (SO_4^{2-}, NO_3^-, Cl^-)

Samples for anion analyses are filtered through Nucleopore 0.4-μm polycarbonate filters, following LTM protocols in Section 2. Anion samples are refrigerated and analyzed as soon as possible.

2.3.3 Filtration and Preservation Protocol for Cation Analyses (Ca, Mg, Na, K, and Al)

Samples for cation, SiO_2, NH_4^+, and total Al analyses are filtered through Nucleopore 0.4-µm polycarbonate filters, following LTM protocols in Section 2. Preservation is by acidification to pH < 2.0 with HNO_3 for cations and Al. Samples for other variables are refrigerated and analyzed as soon as possible.

2.3.4 True Color and DOC

Samples for true color and DOC are filtered through 0.7-µm Whatman GF/F filters. Preservation of DOC aliquots is by acidification to pH < 2.0 with H_2SO_4.

2.4 ANALYTICAL METHODS

See Table 4-1.

2.5 CALIBRATION PROCEDURES

2.5.1 pH

A deionized water blank is used as a standardization check in addition to the suggested checks in the protocol. The air-equilibrated sample is not stirred in addition to the aeration.

3.2 PROCEDURES FOR ASSESSING PRECISION AND ACCURACY

3.2.2 Analytical Precision

Two laboratory duplicates (splits) are analyzed each season, with at least 10% analytical replication.

3.2.3 Sampling and Analysis Precision

Two field collocated samples are analyzed each season.

3.2.4 Accuracy and Bias

Several internal QC samples, and at least one NIST (formerly NBS) or EPA reference material sample are analyzed with each batch. One spike sample is also analyzed with each batch. LRTAP and Watershed Manipulation Project audits are also routinely processed by the laboratory.

3.3 DATA VALIDATION AND REPORTING

3.3.1 Cation-Anion Charge Evaluation

A cation-anion ratio is calculated; the range of acceptable ratios is from 0.85 to 1.15 (± 15%). If the ratio exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the ratio is recalculated.

TABLE 4-1. ANALYTICAL METHODS FOR MAINE REGION (through 1989)

Variable	Method/Equipment	Reference
pH, field	Closed-cell pH, measured in lab	Hillman et al., 1986
pH, lab	Aeration with 300 ppm CO_2 air, Both pH measurements made with Orion Ross™ 81-02 combination electrodes and Orion EA 920 meters.	Hillman et al., 1986
ANC	Radiometer ARAS™ autotitrators, Gran plot titrations to pH 3.5	Hillman et al., 1986
Conductivity	YSI model 35 meter	U.S. EPA, 1983
Cl^-, NO_3^-, SO_4^{2-}	Dionex 2120i, with integrators and autosamplers.	Hillman et al., 1986
Ca, Mg, Na, K	Perkin-Elmer 703 AAS, Ca and Mg with N_2O-acetylene flame; Na and K with air-acetylene flame.	U.S. EPA, 1983
Al, total dissolved	Perkin-Elmer 3030B HGA AAS, with autosampler.	Hillman et al., 1986
DOC	OI Model 700 Infrared Spectrometer, with autosampler.	OI standard methods
SiO_2, NH_4^+	Technicon TRAACS 800, with autosampler.	U.S. EPA, 1983 Hillman et al., 1986
True color	Bausch & Lomb Spectronics 70.	U.S. EPA, 1983

Samples in excess of +10% and -5% receive special scrutiny to ascertain whether a reasonable explanation exists for the discrepancy.

3.3.2 Specific Conductance Evaluation

A conductance ratio is calculated, and the range of acceptable ratios is from 0.80 to 1.20. If the ratio exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the ratio is recalculated. Maine LTM samples are in the 20 to 30 µS/cm range.

SECTION 5
VERMONT REGION

This section contains information about specific procedures and methods used in the Vermont region through 1989 and was prepared by Jim Kellogg and Doug Burnham of the Vermont Department of Environmental Conservation, 103 South Main Street, Waterbury, Vermont, 05676. This information supplements the information in Sections 1 to 3, thus only sections in which region-specific information is required are listed. These sections include project organization and responsibilities (1.2), sample containers (2.1), filtration and preservation protocols (2.3.2 to 2.3.4), analytical methods (2.4), calibration procedures (2.5), procedures for assessing precision and accuracy (3.2.2 to 3.2.4), and data validation criteria (3.3.1 and 3.3.2). The following section numbers and titles in italics correspond to numbers in Sections 1 to 3.

1.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

Wallace McLean, Project Officer	-	Administrative overview and management.
Douglas Burnham, Project Supervisor	-	Administrative support and supervision of project manager.
James Kellogg, Project Manager	-	Manages and conducts program operations: field, analytical, data management, report writing, QA/QC, etc.
Gail Center, Project Technician	-	Assists project manager in all aspects of project implementations.
Brenda Clarkson, Data Management and Statistician	-	Administrative and technical support for data management, QA/QC, data analysis, statistics, etc.
Water Quality Division Staff	-	Laboratory services for chemical and biological analyses, secretarial services, and other project support as needed.

2.1 SAMPLE CONTAINERS: CLEANING AND CONDUCTIVITY CHECKS

The following information is reported directly from the Vermont Laboratory Glassware Washing Procedures Manual - June 1987: Acid Deposition Lake Sampling Containers:

A. 1-liter round Nalgene - pH, alkalinity, apparent color, specific conductance.

B. 125-ml rectangular Nalgene - anions (SO_4^{2-}, Cl^-, NO_3^-) - both bottles are composed of high-density linear polyethylene, with polypropylene caps.

1. Empty and rinse three times with the highest quality deionized water available.

2. Fill with deionized water, cap and allow to stand for 48 hours.

3. After initial cleaning and storage 50% of these bottles are randomly selected for a conductance check. The bottles are slowly rotated so that water touches all surfaces and cap. The conductivity is then checked and if found to be greater than 1.5 µS/cm in any of the checked bottles, all are rerinsed, refilled with deionized water, and retested 48 hours later. This procedure continues until all bottles pass.

   SPECIAL NOTE: No detergent is ever used on these containers.

C. 60- and 125-ml round Nalgene-metals (Al) and cations (Ca, Mg, Na, K). Both bottles are composed of high density linear polyethylene, with polypropylene caps.

1. Empty and rinse three times with the highest grade deionized water available.

2. Rinse three times with 3 N (20%) reagent grade HNO_3 followed by six rinses with deionized water.

3. Fill with deionized and allow to stand for 48 hours.

4. After initial cleaning and storage 50% of these bottles are randomly selected for a conductance check. The bottles are slowly rotated so that the water touches all surfaces and cap. The conductivity is then checked and if found to be > 1.5 µS/cm in any of the checked bottles all are rerinsed and refilled with deionized water and retested 48 hours later. This procedure continues until all bottles pass.

   SPECIAL NOTE: No detergent is ever used and all acid must be rinsed out from these containers.

   A separate notebook is kept with the conductivity meter and is used to record all results pertaining to the conductivities of washed bottles.

2.3 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

2.3.2 Filtration and Preservation Protocol for Anion Analyses (SO_4^{2-}, NO_3^-, Cl^-)

Samples are filtered within 12 hours of sample collection with Gelman GA-6 cellular acetate 0.45-µm filters (47 mm). Filters are rinsed by soaking in DI water; filtration flask and sample containers are rinsed once with filtered water. Anion samples are refrigerated.

2.3.3 Filtration and Preservation Protocol for Cation Analyses (Ca, Mg, Na, K, and Al)

Samples are filtered within 12 hours of sample collection with Gelman GA-6 cellular acetate 0.45-µm filters (47 mm). Filters are rinsed by soaking in DI water; filtration flasks and sample containers are rinsed once with filtered water. Preservation follows LTM protocol in Section 2.

2.3.4 True Color and DOC

Samples for true color are filtered within 12 hours of sample collection with Gelman GA-6 cellular acetate 0.45-µm filters (47 mm). The filtered samples are refrigerated until analyzed.

2.4 ANALYTICAL METHODS

See Table 5-1.

2.5 CALIBRATION PROCEDURES

2.5.1 pH

A fritted glass diffuser is used for the air-equilibrated pH measurement.

2.5.2 Atomic Absorption Spectrophotometer (AAS): Ca, Mg, Na, K, and Al

The AAS is calibrated with four reference standards for graphite furnace, and five reference standards for flame analyses. An EPA QC sample is tested before beginning sample analysis. The standards are rechecked after every 6-10 samples.

2.5.3 Ion Chromatograph (IC): SO_4^{2-}, Cl^-, and NO_3^-

Three IC reference standards are used to calibrate the instrument. Standards are rechecked if more than 10 lake samples are analyzed, although batches generally consist of fewer than 10 samples. One of the three standards are used as a QC check. LRTAP samples are also saved and used as an additional QC check.

2.5.4 Specific Conductance

Two prepared KCl standards with conductivity < 50 µS/cm are tested prior to the analysis of lake samples.

3.2 PROCEDURES FOR ASSESSING PRECISION AND ACCURACY

3.2.2 Analytical Precision

A minimum of 10% analytical duplicates are analyzed for all variables.

3.2.4 Accuracy and Bias

A minimum of 10% of the samples analyzed for anions and cations are spiked samples. The Vermont laboratory participates in the LRTAP studies three times per year, and in the EPA Acid Precipitation Performance Evaluation survey two times per year. Internal checks are conducted four times per year.

TABLE 5-1. ANALYTICAL METHODS FOR VERMONT REGION (through 1989)

Variable	Method/Equipment	Reference
pH, field	Beckman 21 meter with temperature compensation. Sample placed in 30-ml plastic beaker and analyzed.	U.S. EPA, 1983
pH, lab (stirred)	Cole Palmer DigipHase meter, Cole Palmer KCl combination electrode with calomel reference	U.S. EPA, 1983
(bubbled)	Same meter and electrode but the sample is air-equilibrated with 300 ppm CO_2 (Air-equilibrated reported separate from lab pH)	U.S. EPA, 1983
ANC	Titration with 0.020 N H_2SO_4 to pH 3.5, with about 17 points used for Gran plot calculation.	Pfeiffer and Festa, 1980
Conductivity	YSI model 32 with two cells, one for samples < 20 µmhos, another for samples > 20 µmhos.	U.S. EPA, 1983
Cl^-, SO_4^{2-}, NO_3^-	Dionex Ion Chromatograph 2000 with integrator; manual injection, 3 calibration standards with check sample (one of the original standards) run after every 10 samples.	O'Dell, et al., 1984
Ca, Mg, Na, K	Perkin Elmer 3030B; 5 calibration standards; acetylene flame, 1 out of every 10 samples is a duplicate or spike. Lanthanum added to Ca, Mg.	U.S. EPA, 1979 & 1983
Al, total dissolved	Perkin Elmer 3030B and HGA 600 furnace with autosampler	U.S. EPA, 1983
Color	True color is filtered through 0.45-µm filter and measured at 420 nm on a spectrophotometer.	Black & Christman, 1963
	Apparent color is unfiltered and measured on a Taylor color comparator.	U.S. EPA, 1983

3.3 DATA VALIDATION AND REPORTING

3.3.1 Cation-Anion Charge Evaluation

Percent ion difference is calculated, and reanalysis criteria are as follows:

Sum of ions (μeq/L)	% Ion difference
< 50	60
≥ 50 < 100	30
≥ 100	15

If the percent ion difference exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the percent ion difference is recalculated.

3.3.2 Specific Conductance Evaluation

Percent conductance difference is calculated, and reanalysis criteria are as follows:

Measured Conductance (μS/cm)	% Conductance Difference
< 5	> 50
≥ 5 < 30	> 30
≥ 30	> 20

If the percent conductance difference exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the percent conductance difference is recalculated.

SECTION 6
ADIRONDACK REGION

This section contains information about specific procedures and methods used in the Adirondack region through 1989 and was prepared by Charles Driscoll and Rich Van Dreason, Department of Civil Engineering, Syracuse University, Syracuse, New York, 13244. This information supplements the information in Sections 1 to 3, thus only sections in which region-specific information is required are listed. These sections include project organization and responsibilities (1.2), sample containers (2.1), filtration and preservation protocols (2.3.2 to 2.3.4), analytical methods (2.4), calibration procedures (2.5), procedures for assessing precision and accuracy (3.2.2 to 3.2.4), and data validation criteria (3.3.1 and 3.3.2). The following section numbers and titles in italics correspond to numbers in Sections 1 to 3.

1.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

Researchers at Syracuse University will sample and analyze for chemical constituents in 16 lakes in the Adirondack region of New York. Dr. Charles Driscoll of Syracuse University, principal investigator of this project, will have overall responsibility for project measurements, sample custody, and data reporting. A research associate will supervise sample collection, analytical measurements, and sample transfer and handling, as well as data quality and transfer. Their quality assurance responsibilities include:

1. Monitoring daily QA/QC activities.
2. Reviewing laboratory notebooks, instrument performance logs, and QA/QC data on a regular basis.
3. Determining that performance audits, triplicate analyses, and other QA/QC activities are performed.
4. Examining data summaries and calculations.
5. Assisting in trouble-shooting problems.
6. Preparing quarterly QA summaries and reports.
7. Checking that all project personnel are competent to perform analyses.
8. Ensuring that all QA/QC operations are followed.

A field and laboratory technician will be responsible for:

1. Performing collection, including field blanks and replicated samples.
2. Processing aqueous samples for the analysis of major solutes (Table 6-1).
3. Maintaining appropriate notebooks of field activities and the sample log.
4. Observing and recording events that may affect field data.
5. Understanding their role in the project and laboratory.
6. Maintaining appropriate notebooks, instrument logs, and QA/QC records.
7. Observing and recording events that may affect experimental data.
8. Reporting any problems or concerns to the principal investigator.
9. Performing routine maintenance on instrumentation as required.

Regular meetings of project personnel will be held to discuss experimental progress, analytical problems or concerns, or any other problems within the project.

2.1 SAMPLE CONTAINERS: CLEANING AND CONDUCTIVITY CHECKS

All water samples will be collected in prelabelled, HCl-washed (1.0 N) polyethylene containers soaked (> 12 hours) and rinsed (> 5 times) with deionized water. Sample containers will be rinsed three times with sample solution prior to collection.

At least 25% of the cleaned containers will have a specific conductance check. Specific conductance of deionized water in the container will be measured after a 48-hour period. If the specific conductance is greater than 1.5 µs/cm, all the containers in that batch will be rerinsed. The highest conductivity value for each batch will be recorded.

2.3 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

2.3.2 Filtration and Preservation Protocol for Anion Analyses (SO_4^{2-}, NO_3^-, Cl^-)

Samples for anion analyses are transported on ice to the Environmental Engineering Laboratory at Syracuse University, then stored at 4°C until analyzed. These samples are not filtered.

2.3.3 Filtration and Preservation Protocol for Cation Analyses (Ca, Mg, Na, K, and Al)

Samples for cation analyses are transported on ice to the laboratory, stored at 4°C, and not filtered. Samples for Al fractions are processed shortly after collection, then stored at 4°C.

2.3.4 True Color and DOC

Samples for color are not filtered. Samples for DOC analyses are filtered through baked GF/F (0.7 µm) filters, then H_2SO_4 is added.

2.4 ANALYTICAL METHODS

See Table 6-1.

2.5 CALIBRATION PROCEDURES

Calibration procedures follow the protocols in Section 2.

3.2 PROCEDURES FOR ASSESSING PRECISION AND ACCURACY

3.2.2 Analytical Precision

Analytical precision is estimated from laboratory triplicate samples analyzed once during each suite of monthly samples.

TABLE 6-1. ANALYTICAL METHODS FOR ADIRONDACK REGION (through 1989)

Variable	Method/Equipment	Reference
pH, field	Glass body Ross^{TM} combination electrode.	APHA, 1985
pH, lab	Glass body Ross^{TM} combination electrode, Orion 701A, aeration with 300 ppm CO_2.	APHA, 1985 Hillman et al., 1986
ANC	Titration to pH 3.2 with 0.01 N HCl; Gran plot analysis.	Gran, 1952
Conductivity	YSI model 32 meter.	APHA, 1985
Cl^-, SO_4^{2-}, NO_3^-	Dionex ion chromatograph.	Small et al., 1975
Ca, Mg, K, Na	Perkin Elmer 3030B AAS; air-acetylene flame, Ca and Mg with lanthanum addition.	Slavin, 1968
Monomeric Al	Field extraction by 8-hydroxyquinoline into MIBK, analysis by AAS, graphite furnace.	Barnes, 1976
Nonlabile, organic monomeric Al	Fractionation by ion exchange column, analysis for monomeric Al.	Driscoll, 1984
DOC	Dohrman direct injection; UV enhanced persulfate oxidation, CO_2 detection by IR spectrophotometry.	Dohrman, 1984
Dissolved Inorganic Carbon (DIC)	CO_2 detection by infrared (IR) spectrophotometry.	Dohrman, 1984
Dissolved Silica	Heteropoly blue complex colorimetry; Technicon AutoAnalyzer.	U.S. EPA, 1983
NH_4^+	Phenate colorimetry; Technicon AutoAnalyzer.	U.S. EPA, 1983
Total F^-	Potentiometrically with ion selective electrode after TISAB addition.	Orion, 1976
Apparent Color	Colorimetric platinum on unfiltered sample.	U.S. EPA, 1983

3.2.3 *Sampling and Analysis Precision*

Sampling and analysis precision is estimated from the analysis of triplicate samples collected in the field. One field triplicate is collected during each suite of monthly samples.

3.2.4 *Accuracy and Bias*

QC check samples, along with performance evaluation samples (LRTAP and synthetic Al samples), are used to estimate accuracy.

3.3 *DATA VALIDATION AND REPORTING*

3.3.1 *Cation-Anion Charge Evaluation*

Percent ion difference is calculated, and reanalysis criteria are as follows:

Sum of ions (μeq/L)	% Ion difference
< 50	60
≥ 50 < 100	30
≥ 100	15

If the percent ion difference exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the percent ion difference is recalculated.

3.3.2 *Specific Conductance Evaluation*

Percent conductance difference is calculated, and reanalysis criteria are as follows:

Measured Conductance (μS/cm)	% Conductance Difference
< 5	> 50
≥ 5 < 30	> 30
≥ 30	> 20

If the percent conductance difference exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the percent conductance difference is recalculated.

SECTION 7
UPPER MIDWEST REGION

This section contains information about specific procedures and methods used in the Upper Midwest region through 1989 and was prepared by Bruce Holdhusen, Department of Civil and Mineral Engineering, 500 Pillsbury Dr., S.E., Minneapolis, Minnesota, 55455, and Katherine Webster, Wisconsin Department of Natural Resources, 3911 Fish Hatchery Road, Madison, Wisconsin, 53711. This information supplements the information in Sections 1 to 3, thus only sections in which region-specific information is required are listed. These sections include project organization and responsibilities (1.2), sample containers (2.1), filtration and preservation protocols (2.3.2 to 2.3.4), analytical methods (2.4), calibration procedures (2.5), procedures for assessing precision and accuracy (3.2.2 to 3.2.4), and data validation criteria (3.3.1 and 3.3.2). The following section numbers and titles in italics correspond to numbers in Sections 1 to 3.

1.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

Principal investigator, Patrick L. Brezonik, University of Minnesota (UM): project oversight, including oversight of laboratory methods and procedures, laboratory analyses and laboratory personnel; review of data before submittal; review of QA/QC procedures; analysis and interpretation of data set for temporal and spatial trends; preparation and submittal of annual progress reports and completion reports; oral and poster presentations on project at technical meetings and LTM review meetings; preparation of manuscripts on results of study for submission to technical journals; correspondence with co-investigator and with ERL-Corvallis personnel.

Co-investigator, Katherine E. Webster, Wisconsin Department of Natural Resources (WDNR): management of sampling program, including preparation of materials for sampling trips, participation in sampling trips, training of other individuals involved in lake sampling, supervision of field analyses and transfer of samples to analytical laboratory; maintenance of field notes and field data; maintenance of field equipment; preparation of computerized SAS data base for field and laboratory data; preparation of sections of annual progress reports on field aspects of project; review of data for temporal and spatial trends; oral and poster presentations on project at technical meetings and LTM review meetings; preparation of manuscripts on results of study for submission to technical journals; correspondence with ERL-Corvallis personnel regarding data and methodological issues.

Laboratory manager, Bruce Holdhusen, University of Minnesota (UM) (since July 1988): contact person for receipt of lake water samples; supervision of technicians and graduate students who perform various chemical analyses; analysis of lake samples for variety of chemical constituents, including major cations and anions; review and evaluation of analytical methods; direct supervision of QC/QA program and maintenance of records pertaining thereto; review of chemical data for accuracy and precision before being inserted into laboratory computer data base; transfer of data to WDNR for addition to SAS data file; maintenance and update of laboratory manual of procedures; ordering of laboratory supplies; contact person for equipment maintenance.

Various technicians (UM and WDNR) and graduate students (UM only): prepare field materials (e.g., wash sample bottles) and participate in field sampling and field analysis program under direction of field supervisor; prepare solutions and reagents and perform various chemical analyses under direction of laboratory manager; perform routine calculations and enter data into computer data files. Note: names are not included here because personnel change periodically and these individuals report directly to the individuals listed above, who have direct responsibilities for their work.

2.1 SAMPLE CONTAINERS: CLEANING AND CONDUCTIVITY CHECKS

Starting with spring 1989, HCl instead of HNO_3 has been used to clean cation/metals containers as recommended in Section 2. Glass bottles for DOC samples are newly purchased for each sample collection. They are cleaned by rinsing three times with deionized water.

2.3 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

2.3.2 Filtration and Preservation Protocol for Anion Analyses (SO_4^{2-}, NO_3^-, Cl^-)

Aliquots for anions are filtered through 0.4-µm Nuclepore polycarbonate membrane filters. Rinses are as described in the protocol, except that filters are pre-rinsed with 250 mL of deionized water before sample collection begins. Anion aliquots are frozen prior to shipment. They are kept frozen in the laboratory until the day of analysis.

2.3.3 Filtration and Preservation Protocol for Cation Analyses (Ca, Mg, Na, K, and Al)

Aliquots for cations, metals, and silica are filtered through 0.4-µm Nuclepore polycarbonate membrane filters with rinses as described above. Cation/metals aliquots are preserved with Ultrex™ HNO_3 and kept chilled before and during shipment and stored at 4°C until analysis. Silica aliquots are chilled before shipment and stored at 4°C until analysis.

2.3.4 True Color and DOC

Aliquots for DOC are filtered as in Section 2.3.2, chilled prior to and during shipment, and stored at 4°C until analysis. Aliquots for color are not filtered in the field or laboratory but are taken from the unfiltered "physical parameters" bottle, which is chilled before and during shipment and stored at 4°C before analysis. Aliquots for color are centrifuged in an International clinical centrifuge at 3/4 of full speed for 15 minutes and the supernatant is decanted and analyzed for "true" color.

2.4 ANALYTICAL METHODS

See Table 7-1.

2.5 CALIBRATION PROCEDURES

Procedures follow the LTM protocol as described in Section 2.

3.2 PROCEDURES FOR ASSESSING PRECISION AND ACCURACY

3.2.2 Analytical Precision

Analytical precision is determined routinely by analyzing 10% of the samples in duplicate, with a minimum of one per analytical batch, but more typically two or more, depending on size of analytical batch.

3.2.3 Sampling and Analysis Precision

At least 10% of the field samples are collected in duplicate, including at least one duplicate sample for each of the three states in the Upper Midwest LTM region in each sampling season. The field duplicates are analyzed for all chemical variables.

3.2.4 Accuracy and Bias

Samples used to estimate accuracy on a routine basis are from the U.S. EPA (certified analytical reference samples, hereafter referred to as EPA QC standards). These standards are prepared as stock solutions according to directions provided with them, and dilutions are prepared with each analytical run to obtain standards in the approximate range of the lakewater samples in the Upper Midwest LTM program. The EPA QC standards are analyzed at the beginning of each analytical run and after every 10 samples within an analytical run. In addition, laboratory standard solutions are analyzed at the beginning of each analytical run.

TABLE 7-1. ANALYTICAL METHODS FOR UPPER MIDWEST REGION (through 1989)

Variable	Method/Equipment	Reference[a]
pH, field	Orion model 501A, Beckman Futura II Star Series combination electrode	U.S. EPA, 1987
pH, lab	Beckman model 71 meter, Corning combination electrode model 476541; air equilibration with 300 ppm CO_2	U.S. EPA, 1987
ANC	Titration to pH 3.5 with 0.02 N H_2SO_4; Gran plot calculation using all data for pH 4.0 and below to calculate regression line	U.S. EPA, 1987
Conductivity	YSI model 32 conductivity meter	U.S. EPA, 1987
Cl^-, SO_4^{2-}	Dionex model 10 ion chromatograph	U.S. EPA, 1987
NO_3^-	Automated cadmium reduction method on Technicon AutoAnalyzer II	APHA, 1981, 1985
Ca, Mg, Na, K	Flame atomic absorption spectrophotometry with Varian model 1475 AAS; air-acetylene flame for Mg, Na, K; N_2O-acetylene flame for Ca; each calibrated with blank plus five standards	U.S. EPA, 1987
Al, total dissolved	Flameless AAs with Perkin Elmer model 4000 and model 400 HGA and autosampler on filtered samples; calibrated with five standards plus blank	U.S. EPA, 1987
DOC	Dohrman DC-80; direct injection with UV oxidation	U.S. EPA, 1987
SiO_2	Manual heteropolyblue method for reactive silica on Hitachi 100.20 spectrophotometer	APHA, 1981, 1985
NH_4^+	Manual indophenol method on Hitachi 100.20 spectrophotometer (similar to manual method in APHA 1985)	Solorzano, 1969
True color	True color on centrifuged sample; absorbance at 420 nm with 5-cm cells on Beckman model 26 with calibration curve prepared using standard chloroplatinate solution. Method is similar to that of EPA (1987) and APHA (1985) except that a spectrophotometer is used to quantify absorbance at a specific wavelength rather than estimating color by visual comparison with standards.	None

[a] Instrument manuals of the manufacturers of the cited instruments are additional references for cations, anions, and DOC.

The analytical laboratory also participates in the LRTAP Interlaboratory Comparability Studies three times per year to evaluate laboratory bias, and analyzes synthetic audit samples when provided by the U.S. EPA-Las Vegas laboratory for aluminum analyses.

3.3 DATA VALIDATION AND REPORTING

3.3.1 Cation-Anion Charge Evaluation

Percent ion difference is calculated, and reanalysis criteria are as follows:

Sum of ions (μeq/L)	% Ion difference
< 50	20
≥ 50 < 100	10
≥ 100	10

If the percent ion difference exceeds these values, the data are first reviewed to determine whether there are any transposition recording or calculation errors, then the data for each variable are examined for possible analytical error. Larger anion deficits than the criteria allow may not trigger re-analysis for a few lakes with high color, for which such deficits occur consistently and thus are not indicative of analytical errors. Any suspect variables are reanalyzed, and the percent ion difference is recalculated.

3.3.2 Specific Conductance Evaluation

Percent conductance difference is calculated, and reanalysis criteria are as follows:

Measured Conductance (μS/cm)	% Conductance Difference
< 5	No samples in this category
≥ 5 < 30	25
≥ 30	20

If the percent conductance difference exceeds these values, the data are first reviewed to determine whether there are any transposition recording or calculation errors, then the data for each variable are examined for possible analytical error. Larger anion deficits than the criteria allow may not trigger re-analysis for a few lakes with high color, for which such deficits occur consistently and thus are not indicative of analytical errors. Any suspect variables are reanalyzed, and the percent conductance difference is recalculated.

SECTION 8
COLORADO REGION

This section contains information about specific procedures and methods used in the Colorado region through 1989 and was prepared by John Turk and Don Campbell, U.S. Geological Survey, Bldg. 53, MS 415, Denver Federal Center, Lakewood, Colorado, 80225. This information supplements the information in Sections 1 to 3, thus only sections in which region-specific information is required are listed. These sections include project organization and responsibilities (1.2), sample containers (2.1), filtration and preservation protocols (2.3.2 to 2.3.4), analytical methods (2.4), calibration procedures (2.5), procedures for assessing precision and accuracy (3.2.2 to 3.2.4), and data validation criteria (3.3.1 and 3.3.2). The following section numbers and titles in italics correspond to numbers in Sections 1 to 3.

1.2 PROJECT ORGANIZATION AND RESPONSIBILITIES

This project is a cooperative effort of the U.S. Geological Survey, the U.S. Environmental Protection Agency, and the Colorado Department of Health. John Turk, USGS principal investigator, has responsibility for project design, contracting of outfitters, laboratory analysis, quality assurance, training, safety, and report preparation.

2.1 SAMPLE CONTAINERS: CLEANING AND CONDUCTIVITY CHECKS

All containers are obtained from the USGS-CAL (Central Analytical Laboratory) in Arvada, Colorado. New lots of sample containers are prepared by the CAL as follows: bottles for DOC are fired, bottles for cation and metals determination are washed in nitric acid and rinsed with deionized water, bottles for nutrients and anions are soaked for at least three days in deionized water.

2.3 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

2.3.2 Filtration and Preservation Protocol for Anion Anlyses (SO_4^{2-}, NO_3^-, Cl^-)

Anions are measured on aliquots filtered through Gelman 0.45-µm cellulose acetate filters.

2.3.3 Filtration and Preservation Protocol for Cation Anlyses (Ca, Mg, Na, K, and Al)

Cations are measured on aliquots filtered through Gelman 0.45-µm cellulose acetate filters and preserved with concentrated nitric acid, provided in ampoules and documented by the CAL.

2.3.4 *True Color and DOC*

True color is measured on aliquots filtered through Gelman 0.45-µm cellulose acetate filters. DOC is measured on aliquots filtered through 0.4-µm Selas sintered silver filters.

2.4 *ANALYTICAL METHODS*

See Table 8-1.

2.5 *CALIBRATION PROCEDURES*

Calibration procedures follow the protocols outlined in Section 2.

3.2 *PROCEDURES FOR ASSESSING PRECISION AND ACCURACY*

3.2.2 *Analytical Precision*

Analytical duplicates are prepared by the CAL, with at least one set of duplicates in each batch.

3.2.3 *Sampling and Analysis Precision*

On each sampling trip, a field duplicate is prepared and submitted as a regular sample. These data are stored as routine samples but keyed with a 5-minute difference in time from the regular sample.

3.2.4 *Accuracy and Bias*

Laboratory accuracy is addressed by the CAL with the use of QC check samples and control charts. Audit samples provided by the EPA are submitted to the laboratory.

3.3 *DATA VALIDATION AND REPORTING*

3.3.1 *Cation-Anion Charge Evaluation*

A cation-anion ratio is calculated; the range of acceptable ratios is from 0.85 to 1.15 (± 15%). If the ratio exceeds these values, the data for each variable are examined for possible analytical error. The most likely anomalous constituents are selected by comparison to previously validated data, then any suspect variables are reanalyzed, and the ratio is recalculated. If the rerun value does not meet the check stated above, a new analysis is run from an archived sample.

TABLE 8-1. ANALYTICAL METHODS FOR COLORADO REGION (through 1989)

Variable	Method/Equipment	Reference
pH, field	Glass body Ross™ Combination Electrode	Turk, 1986
pH, lab	Glass body Ross™ Combination Electrode	Fishman et al., 1985
ANC	Titration to pH 3.0 with 0.01639 N H_2SO_4 Gran function endpoint	Stumm and Morgan, 1981
Conductivity	YSI 32 meter	Fishman et al., 1985
Cl^-, SO_4^{2-}, NO_3^-, F^-	USGS Arvada Lab, Dionex IC	"
Ca, Mg	USGS Arvada Lab, ICP	"
Na, K	USGS Arvada Lab, Low level AAS	"
Al, total dissolved	USGS Arvada Lab, DC plasma spectrometer	"
DOC	USGS Arvada Lab, UV oxidation, Dohrman (method used as presented in operating manual for instrument; being prepared as USGS method)	"
DIC	USGS Arvada Lab, Dohrman	"
Si	USGS Arvada Lab, ICP	"
NH_4^+	USGS Arvada Lab, Technicon AutoAnalyzer	"
True Color	USGS Arvada Lab, Comparator	"

3.3.2 *Specific Conductance Evaluation*

If the difference between measured and calculated specific conductance is > 20%, the analysis is assumed to be in error for at least one major ion or for specific conductance. Specific conductance is rerun; if this does not correct the imbalance, the ion concentrations are compared to previously validated data. Suspect variables are reanalyzed as in Section 3.3.1.

SECTION 9
CATSKILL REGION

This section contains information about specific procedures and methods used in the Catskill region through 1989 and was prepared by Peter Murdoch, U.S. Geological Survey, Water Resources Division, Box 1397, Room 348, Albany, New York, 12201. This information supplements the information in Sections 1 to 3, thus only sections in which region-specific information is required are listed. These sections include project organization and responsibilities (1.2), sample containers (2.1), filtration and preservation protocols (2.3.2 to 2.3.4), analytical methods (2.4), calibration procedures (2.5), procedures for assessing precision and accuracy (3.2.2 to 3.2.4), and data validation criteria (3.3.1 and 3.3.2). The following section numbers and titles in italics correspond to numbers in Sections 1 to 3.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

Project Leader: Peter S. Murdoch, U.S. Geological Survey, Water Resources Division, Albany, New York

Field Coordinator: Antony J. Ranalli

Laboratory Coordinator: Debra Horan-Ross

Laboratories	Analyst	Constituents
USGS-Albany	D. Horan-Ross	Anions, ANC, conductance, pH
NYC-Valhalla	R. Corradi	Aluminum, silica
NYC-Grahamsville	S. Schindler	DOC, cations
USGS-Frost Valley	C. Swain	Field pH

2.1 SAMPLE CONTAINERS

Anion, pH, ANC, conductance, and silica aliquot containers are rinsed with deionized water and soaked for 48 hours at the USGS-CAL (Central Analytical Laboratory) in Arvada, Colorado. These bottles are used only once and are rinsed three times with filtered sample before filling.

Cation and aluminum aliquot containers are acid rinsed at the USGS-CAL in Arvada, Colorado. These containers are also used only once and rinsed three times with filtered sample before filling.

DOC aliquot containers are rinsed with tap water, then rinsed with a 25% nitric acid solution before a 24-hour soak with a dilute nitric acid solution. The bottles are then rinsed four times with deionized water, capped and stored wet.

2.3 SAMPLE CUSTODY, PREPARATION, AND PRESERVATION

2.3.2 Filtration and Preservation Protocol for Anion Analyses (SO_4^-, NO_3^-, Cl^-)

Anion aliquots are filtered within 24 hours of collection through 0.4-μm Nucleopore polycarbonate filters and refrigerated for analysis within 14 days of collection. Before September 1988, anion aliquots were filtered through 0.1-μm Nucleopore polycarbonate filters.

2.3.3 Filtration and Preservation Protocol for Cation Analyses (Ca, Mg, Na, K, and Al)

Aliquots for Ca, Mg, Na, and K are filtered within 24 hours of collection through 0.4-μm Nucleopore polycarbonate filters, acidified with ultra-pure nitric acid, and stored for analysis within one month of collection. Before September 1988, these aliquots were filtered through 0.1-μm Nucleopore polycarbonate filters. Aluminum aliquots are filtered immediately in the field through 0.1-μm Nucleopore polycarbonate filters and acidified with ultra-pure nitric acid for analysis within one month.

2.3.4 True Color and DOC

DOC aliquots are filtered through 0.4-µm Nucleopore polycarbonate filters and chilled for analysis within two weeks.

2.4 ANALYTICAL METHODS

See Table 9-1.

2.5 CALIBRATION PROCEDURES

Calibration procedures follow the protocols described in Section 2. A low conductance standard (approximately 15 µS/cm) is used in addition to a 50 µS/cm standard.

3.2 PROCEDURES FOR ASSESSING PRECISION AND ACCURACY

3.2.2 Analytical Precision

The Catskill LTM program utilizes laboratory split samples from the same aliquot bottle (10% of samples), QC samples provided by the EPA, and QC samples provided by the USGS to assess analytical precision.

TABLE 9-1. ANALYTICAL METHODS FOR CATSKILL REGION (through 1989)

Variable	Method/Equipment	Reference
pH, field	Glass body Ross™ combination electrode	APHA, 1985
pH, lab	Beckman Model 071 meter; Ross™ combination epoxy body electrode; do not aerate because have found no difference between aerated and nonaerated pH measurement for streams.	APHA, 1985
ANC	Radiometer ABU93 autotitrator with SAC8O sample changer; titrations to pH 3.6, use at least 4 points under pH 5.0 for Gran analysis.	Gran, 1952
Conductivity	Altex (Beckman) meter and probe. Use USGS standards.	APHA, 1985
Cl^-, SO_4^{2-}, NO_3^-	Dionex 2000 with autosampler. Filtered with 0.4-μm filter.	Small et al., 1975
Ca, Mg, Na, K	NYCDEP Grahamsville lab, Perkin Elmer 3030. Atomic absorption spectrophometer (AAS), multiple standard calibrations. Before Oct. 1988, analyzed at USGS Central Analytical Lab (CAL) - Arvada.	Slavin, 1968
Al, total dissolved	NYCDEP Valhalla lab with furnace atomic absorption spectrophotometer (AAS). Filtered with 0.1-μm filter.	Driscoll, 1984
DOC	NYCDEP Grahamsville lab; filtered with 0.4-μm polycarbonate filter; Dohrman direct injection.	Dohrman, 1984
SiO_2	NYCDEP Valhalla laboratory. Colorimetric, silico-molybdate, spectrophotometer. Before Oct. 1988, analyzed at USGS-CAL.	U.S. EPA, 1979

3.2.4 Accuracy and Bias

The Catskill LTM program uses QC check solutions, standard reference materials, performance evaluation samples (both the USGS and LRTAP audit samples), synthetic audit samples, and spike samples for cations and aluminum.

3.3 DATA VALIDATION AND REPORTING

3.3.1 Cation-Anion Charge Evaluation

A cation-anion ratio is calculated, and reanalysis criteria are as follows:

Sum of ions (μeq/L)	Range of acceptable ion ratios
< 50	0.7 - 0.30
≥ 50 < 100	0.85 - 1.30
≥ 100	0.80 - 1.10

If the ratio exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the ratio is recalculated. Data entries are reviewed by a project person other than the one who entered the data to ensure data have been properly entered.

3.3.2 Specific Conductance Evaluation

A conductivity ratio is calculated, and reanalysis criteria are as follows:

Measured Conductance (μS/cm)	Range of acceptable conductivity ratios
< 5	0.7 - 1.30
≥ 5 < 30	0.85 - 1.15
≥ 30	No samples in this category

If the ratio exceeds these values, the data for each variable are examined for possible analytical error. Any suspect variables are then reanalyzed, and the ratio is recalculated.

SECTION 10

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APPENDIX A[1]
WORKING PROTOCOL FOR SAMPLING, SAMPLE ANALYSIS, AND QA/QC FOR THE USEPA LONG-TERM SURFACE WATER MONITORING PROGRAM

May 1985

INTRODUCTION

An EPA program for long-term monitoring of lakes and streams was initiated in 1982 within the NAPAP organizational framework. An ad hoc committee, with representation from USEPA, USGS, TVA, USD-FS, USFWS, USNPS, and Brookhaven National Laboratory, developed a draft sampling and analysis protocol to standardize monitoring efforts among the member Task Group E agencies. This document, with periodic reviews and updates, has served as the standard protocol for the EPA surface water monitoring program since its inception.

In 1984, EPA initiated the National Surface Water survey (NSWS). This three-phase program is scheduled to culminate in the selection of geographically representative lakes for long-term monitoring in the east, upper midwest, and mountainous west. This third phase of NSWS is expected to subsume the existing sites are probably compatible with Phase II owing to their location in low alkalinity regions and their positioning with respect to minimization of extraneous effects that could compromise interpretations of observed changes or trends.

The methods manual developed for NSWS (Hillman et al., 1986) has been used, together with the Task Group E sampling and analysis protocol document, to produce the present "working protocol" for the Long-Term Monitoring Project. Laboratory analytical methodology, detection limits, and QA/QC procedures are more adequately and precisely specified; site selection criteria are not included. The objective has been to align the long-term monitoring methodology with that of NSWS, without undue disruption of existing monitoring procedures. The present document replaces the Task Group E protocol (Aquatic Effects Task Group, March 1984 revised) as the procedural document for the EPA monitoring program. Participating agencies and institutions must be able to demonstrate their use of these or equivalent sampling, analysis, and QA/QC procedures. Audits will be conducted to determine compliance with these procedures.

This document recognizes that U.S. Geological Survey protocols used in their stream research and monitoring program are not necessarily identical with those set forth here. By prior agreement with the EPA project officer, USGS protocols are acceptable in the existing cooperative EPA-USGS stream studies. Differences are few, and are noted where appropriate in this document. The USGS laboratory at Denver, where samples from the cooperative studies are analyzed, is a participant in the NSWS. Therefore, there should be no differences in laboratory analytical methodology.

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[1] This appendix contains the QA plan and sampling methods that were used by LTM cooperators from May 1985 until the current QA Plan (this document) was completed in February 1989.

1.0 COLLECTION OF SAMPLES IN THE FIELD

1.1 Lakes

Lakes should be sampled near their deepest points (at least 20 m from shore if possible). If the water column is not thermally stratified, one sample should be collected approximately one-half meter beneath the water surface. If the water body is stratified, one sample should be collected approximately one-half meter beneath the water surface and a second sample one or two meters above the bottom. These two samples should not be mixed or composited. A plastic closing sampling device of the Van Dorn type should be used to obtain samples at depth; do not use a metal sampler. Samples should be collected from the sampling device in plastic bottles that have been treated as described in 3.0. (See 6.1 regarding replicate samples.)

1.2 Streams

Samples are obtained by hand as near mid-stream as possible, using a properly cleaned and rinsed plastic container of appropriate size. (See 6.1 regarding replicate samples.) Keep hands away from the mouth of the container, and minimize the number of people handling the samples.

1.3 Carefully record any observed conditions that might affect analysis or interpretation of samples in field notes or sampling log.

1.4 Key project personnel who are responsible for sample integrity must be identified.

2.0 MEASUREMENTS

A set of "core" measurements are specified for the EPA monitoring program. These measurements, which are considered to provide sufficient characterization of stream or lake water quality for assessment of sensitivity and changes related to acidification, are:

pH (field and laboratory air equilibrated)
total alkalinity
specific conductance
temperature
Secchi disk transparency (lakes)
true color
major cations (Ca, Mg, Na, K)

major anions (SO_4, NO_3, Cl)
total aluminum (filtered)

Additional measurements, including titrated acidity, DIC, DOC, F^-, Fe, Mn, NH_4, SiO_2, and total P, are being made by the NSWS; some of these analyses, while not required, are also being made by some cooperators in the monitoring program.

Care must be taken to assure that the highest quality deionized water is used throughout all stages of sampling and analysis. Specific conductance of such water should not exceed 1.0 S/cm.

3.0 SAMPLE CONTAINERS

3.1 Type

Containers should be composed of high-density, linear polyethylene, with polypropylene caps (do not use polyseal caps).

3.2 Cleaning of Plastic Containers

3.2.1 Containers to be used for pH, acidity, alkalinity, and anion determinations will be rinsed three times with deionized water, filled with deionized water, and allowed to stand for 48 hours, then emptied and sealed in clean plastic bags until used in the field.

3.2.2 Sample containers for cations and metals will be rinsed three times with deionized water, rinsed three times with 3N HNO_3 (prepared from Baker Instra-Analyzed HNO_3 or equivalent), then rinsed six times with deionized water. They will then be filled with deionized water and allowed to stand for 48 hours. They are then emptied, capped, and placed in clean plastic bags.

3.2.3 After the initial cleaning, 5% of the containers will be checked by filling with deionized water, capping, and slowly rotating the container so water touches all surfaces. Check conductivity; if greater than 1 μS/cm in any of the checked containers, rerinse all containers and retest 5%.

4.0 SAMPLE FILTRATION

4.1 For <u>anion analysis</u> (including SO_4, NO_3, Cl): Rinse a cleaned 250-mL bottle three times with sample water which has been filtered directly into the sample bottle (discarding each rinse). Then fill

to 250 mL with filtered sample. Use a 0.45-μm pore size membrane filter (e.g., Nucleopore polycarbonate or cellulose acetate). Ice or refrigerate. A good portable unit for filtering samples at field sites is described by Kennedy et al., 1976.

4.2 For metals and cation analyses (including Ca, Mg, Na, K): Filter 100 mL of sample into an acid-washed bottle (see 3.2.2) after rinsing three times by passing 100 mL of sample through a 0.45-μm filter and discarding each rinse. Add a 1-mL ampoule of concentrated ultrapure nitric acid (Baker Ultrex or equivalent) to the sample. Ice or refrigerate.

4.2.1 U.S. Geological Survey presently uses 0.1-μm filters for Al, Fe, and Mn in their stream work. (They are conducting comparisons of various pore sizes.)

4.3 Samples for pH, alkalinity, specific conductance, and true color are not filtered.

5.0 SAMPLE PRESERVATION AND MAXIMUM HOLDING TIMES

5.1 Refrigeration at 4°C is the only recommended method of preservation for the following constituents. (Maximum allowable holding times appear in parentheses.) For present purposes, icing must be considered equivalent to 4°C refrigeration.

specific conductance (14 days)

color (48 hours)

pH (no approved holding time; field sample should be analyzed immediately, and air-equilibrated laboratory samples as soon as possible)

alkalinity (14 days, according to NSWS protocol

sulfate (28 days)

chloride (28 days)

silica (28 days)

nitrate-nitrogen (7 days)

5.2 Refrigeration at 4°C plus acidification with nitric acid to pH < 2.0 is recommended for the following constituents:

calcium (6 months)

magnesium (6 months)

sodium (6 months)

potassium (6 months)

aluminum (6 months)

5.3 Labels on all containers should include sufficient information to permit tracing the sample back to point and time of collection.

6.0 QA/QC SAMPLES: LAKES

Replicate samples, filtration blanks, and container blanks (total of four additional samples) are to be obtained once for approximately every 10 lakes sampled, as described in 6.1, 6.2, and 6.3. These are minimum requirements. For each project, this results in the following:

Project	No. of Rep/Blank Sets Per Sampling Interval*	Per Year
University of Minnesota	3 (1/state)	9
University of Maine	1	3
Vermont	2	8
Syracuse University	2	8
TVA	1	4
USGS Colorado	2	6

* Sampling intervals are: Minnesota, Maine - spring, summer, fall; Vermont, TVA - spring, summer, fall, winter; Syracuse - quarterly (17 lakes are sampled monthly, 2 rep/blank sets per quarter); Colorado - monthly, summer only.

6.1 Replicate Samples

Obtain a replicate sample by repeating step 1.1 or 1.2. These replicate samples are analyzed to determine the adequacy of the sampling process in obtaining a representative sample of the lake or stream at a particular point in time.

6.2 Filtration Blanks

Prepare two filtration blanks by filtration of deionized water into properly cleaned (1) anion container (3.2.1) and (2) cation container (3.2.2). Analysis of the filtrate for the appropriate ions determines the adequacy of the filtration process and the cleanliness of the sample containers.

6.3 Container Blanks

Prepare one unfiltered container blank by filling a properly cleaned container (see 3.2.1) with deionized water. Analysis of this sample for pH, alkalinity, specific conductance, and strong/weak acidity (if applicable) provides a check on the adequacy of the container.

6.4 EPA-USGS Cooperative Stream Monitoring Projects

Replicate samples, filtration blanks, and container blanks will be taken at the primary (intensive) stream site each time that site is sampled. In addition, replicates will be obtained on two satellite streams three times yearly under low, intermediate, and high flow conditions.

7.0 MEASUREMENT METHODS

7.1 pH

7.1.1 Field Measurement

Measure as soon after collection as possible. pH should be measured to ± 0.02 units using a high-quality pH meter with an expanded or digital scale. A good electrode is the Corning No. 476182 glass combination or the Ross Model 81-02. The electrode should be calibrated in the field in pH 4.0 and 7.0 buffer solutions and checked with a sulfuric acid solution with a theoretical pH of 4.0 (5×10^{-5} molar H_2SO_4). Rinse probe copiously with sample or deionized water and immerse in the sample. Do not stir. The electrode should remain in the sample until there is no discernible drift in the pH reading, but no longer than 15 minutes. At least 10% of the samples must be measured in replicate. Upon completion of measurement of a sample batch, recheck the pH of the acid solution.

7.1.2 Laboratory (Air Equilibrated) Measurement

For normalization of pH values obtained by various participating investigators, air-equilibrated pH measurements should be obtained in the laboratory. Equilibration is achieved by bubbling samples with standard air containing 300 ppm CO_2 for 20 minutes while stirring on a magnetic stirrer. Use an acid-washed (see 3.2.2) fritted glass diffuser for dispersal of air in the sample. Measure pH immediately following equilibration, following the procedure in 7.1.1. At least 10% of the samples must be measured in replicate (Hillman et al., 1986).

7.2 Specific Conductance (µS/cm at 25°C)

Measured in the laboratory using a wheatstone bridge type conductivity meter. See 8.2 for calibration and QA/QC instructions (Hillman et al., 1986).

7.3 True Color

Comparison of centrifuged sample with platinum-cobalt color standards (U.S. EPA, 1979).

7.4 Total Alkalinity

Titration with 0.020 NH_2SO_4 using Gran plot calculations. Fixed endpoint titration is not acceptable (Gran, 1950, 1952; Golterman and Clymo, 1969; Zimmerman and Harvey, 1978-1979; Hillman et al., 1986).

7.5 Calcium, Magnesium, Sodium, and Potassium

Atomic absorption spectrometry, direct aspiration (U.S. EPA, 1979).

7.6 Sulfate, Chloride, Nitrate

Ion chromatography (Hillman et al., 1986).

7.7 Aluminum, Total Filtered

Graphite furnace atomic absorption (EPA Method 202.2) (Hillman et al., 1986; U.S. EPA, 1979).

7.8 Phosphorus, Total

Colorimetric, automated, block digestor AAII (U.S. EPA, 1979), or USGS colorimetric, phosphomolybdate, automated (Hillman et al., 1986).

7.9 Ammonium

Colorimetric, automated phenate (U.S. EPA, 1979).

7.10 Kieldahl Nitrogen

Colorimetric, automated phenate (U.S. EPA, 1979).

7.11 Table 1 states desired minimum analytical detection limits and within-laboratory relative precision goals.

8.0 QUALITY CONTROL PROCEDURES

Procedures normally followed by participants in the Long-Term Monitoring Project should be continued. The intent of this section is to ensure the common use of standardized quality control

Table 1. Required Minimum Analytical Detection Limits, Within-Laboratory Relative Precision, and Bias Limits[a]

Parameter[b]	Units	Required Detection Limit	Intralab Relative Precision Goal (%)[c]	Bias Upper Limit (%)
Acidity	μeq/L	5	10	10
Alkalinity	μeq/L	5	10	10
Al, total	mg/L	0.005	10 (Al>0.01) 20 (Al<0.01)	10/20
Ca	μeq/L	0.5	5	10
Cl^-	μeq/L	0.3	5	10
Color	ALPH units	0	$\pm$ 5[d]	--
DIC	mg/L	0.05	10	10
DOC	mg/L	0.1	5 (DOC>5) 10 (DOC<5)	10
F^-	μeq/L	0.3	5	10
Fe	mg/L	0.01	10	10
K	μeq/L	0.3	5	10
Mg	μeq/L	0.8	5	10
Mn	mg/L	0.01	10	10
Na	μeq/L	0.4	5	10
NH_4	μeq/L	0.6	5	10
NO_3	μeq/L	0.1	10	10
pH, field	pH units	--	$\pm$ 0.1[d]	--
pH, lab	pH units	--	$\pm$ 0.05[d]	--
SiO_2	mg/L	0.05	5	10
SO_4^{2-}	μeq/L	1.0	5	10
Specific conductance	μS/cm	--[e]	1	5
Total P	mg/L	0.002	10 (P>0.01) 20 (P<0.01)	10/20

[a] Some listed measurements may not apply to the existing Long-Term Monitoring Project (see 2.0).
[b] Dissolved ions and metals are determined, except where noted.
[c] Unless otherwise noted, this is the relative precision at concentrations above about 10 times instrumental detection limits.
[d] Absolute precision goal in terms of applicable units.
[e] Blank must be < 1.0 μS/cm.

procedures for comparability of results. Any of the procedures given here that are not now being followed by cooperating agencies or institutions should be added to their QA/QC programs.

8.1 Precision and Accuracy

8.1.1 Precision

8.1.1.1 Definition

Precision is a measure of agreement among individual measurements of the same property, under prescribed similar conditions. In this project, we recognize (1) intralaboratory precision and (2) sampling and analysis precision.

8.1.1.2 Intralaboratory Precision

Intralaboratory precision is determined by analyzing an individual sample in replicate. This should be done for at least one sample per batch for each variable being measured. The difference between the two resultant values is multiplied by 0.89 to approximate the standard deviation. The standard deviation divided by the mean of the duplicate values and multiplied by 100 yields the relative standard deviation (RSD) in percent. The RSD is an operational statistic (also called the coefficient of variation) indicating the dispersion of a set of replicate measurements as a percentage of the mean value. In reporting precision for a given variable, show the number of replicate analyses, range of RSD values, and average RSD.

8.1.1.3 Sampling and Analysis Precision

Sampling precision cannot be estimated directly. However, the precision in the combined sampling and analysis procedure can be estimated from the analysis of the duplicate samples taken in the field (see 6.1). Then the sampling variance can be estimated by subtracting the analytical variance obtained in 8.1.1.2. The precision in the combined sampling and analysis operation is estimated by applying the same methodology described for intralaboratory precision (8.1.1.2).

8.1.2 Accuracy

8.1.2.1 Definition

Accuracy is a measure of the closeness of an individual measurement or an average of a number of measurements to the true values. Accuracy includes both precision and recovery and can be expressed as a percent recovery or percent bias interval.

8.1.2.2 Evaluation of Accuracy

Two approaches are specified:

8.1.2.2.1 Fortify an actual sample with a known amount of material, analyze the fortified (spiked) sample, and calculate the percent recovery. This should be done for at least one sample per batch for each variable being measured. In reporting accuracy for a given variable, show the number of spiked analyses, concentration of spike, range of bias (+ and – percent), and average bias (+ or – percent).

8.1.2.2.2 Audit samples are provided three times each year by an independent contractor. Analysis results are compared with the known concentrations to determine (1) intralaboratory bias and (2) comparability of measurements among the various monitoring projects.

8.2 Cautions Regarding Specific Conductance and Alkalinity

8.2.1 Specific Conductance

After calibration and before measuring the first sample, measure the conductance of a QC standard. The standard should have a theoretical or certified conductance of about 50 μS/cm (0.00050000 M KCl has a conductance of 73.90 μS/cm at 25°C). It must be prepared from a stock solution that is different from that from which the calibration standard is prepared. If the measured conductivity is not within ± 1% of the certified value, then restandardize the meter and cell and repeat the measurement.

Remeasure the conductance of the QC standard at least once every 10 samples. One sample per batch must be measured in duplicate.

8.2.2 Alkalinity

At least 10% of alkalinity titrations must be run in replicate. Agreement must be ± 10% or less. If not, run a third determination.

8.3 Further Procedural Checks

Once each variable in a sample has been determined, there are several procedures which must be followed to check the correctness of the analyses. These are outlined below.

8.3.1 Cation-Anion Balance

Theoretically, the sum of equivalents of anions equals the sum of equivalents of cations in a sample. In practice, this rarely occurs due to analytical variability and ions which are present but not measured. For each sample, the sums of the measured anion and cation equivalents, total ion strength, and ion percent difference are calculated as follows:

$$\Sigma \text{ anions} = [Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}] + [HCO_3^-] + [CO_3^{2-}]$$

$$\Sigma \text{ cations} = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+] + [H^+]$$

$$\% \text{ ion difference} = \frac{\Sigma \text{ anions} - \Sigma \text{ cations}}{\Sigma \text{ anions} + \Sigma \text{ cations}} \times 100$$

$$\text{Total ion strength} = \Sigma \text{ anions} + \Sigma \text{ cations}$$

Omission of F^-, CO_3^{2-}, and NH_4^+ will not significantly affect results. Alkalinity plus H^+ (calculated from pH) may be used for HCO_3^-.

All concentrations are expressed as microequivalents/liter (μeq/L). Table 2 lists factors for converting mg/L to μeq/L for each of the parameters.

Samples that have a poor ion balance may have to be reanalyzed. Table 3 lists the reanalysis criteria.

8.3.2 Specific Conductance Balance

An estimate of the specific conductance of a sample can be calculated by summing the equivalent conductance values for each measured ion at infinite dilution.

The calculated conductance is determined by multiplying the concentration for each ion (in μeq/L) by the appropriate factor (F) in Table 4.

The calculated conductance for the entire sample is obtained from the relationship,

$$\text{Calculated conductance} = \frac{\Sigma \text{ (F x Conc. in } \mu\text{eq/L)}}{1000} \times 100$$

The percent difference between measured conductance and calculated conductance if given by:

$$\% \text{ conductance difference} = \frac{\text{Calculated} - \text{Measured}}{\text{Measured}} \times 100$$

Samples that have percent conductance differences exceeding the limits listed in Table 3 may have to be reanalyzed.

Table 2. Factors to Convert mg/L to μeq/L

Ion	Factor (μeq/L per mg/L)
Ca^{2+}	49.9
Cl^{-}	28.2
CO_3^{2-}	33.3
F^{-}	52.6
K^{+}	25.6
Mg^{2+}	82.3
Na^{+}	43.5
NH_4^{+}	55.4
NO_3^{-}	16.1
SO_4^{2-}	20.8
Alkalinity (as $CaCO_3$	20.0

Table 3. Chemical Reanalysis Criteria

A.	Cation-Anion Balance	
	Total Ion Strength (μeq/L)	% Ion Difference[a]
	< 50	> ± 60
	≥ 50 < 100	> ± 30
	≥ 100	> ± 15
B.	Calculated vs. Measured Conductance	
	Measured Conductance (μS/cm)	% Conductance Difference[a]
	< 5	> 50
	≥ 5 < 30	> 30
	≥ 30	> 20

[a] If the percent difference exceeds these values, the sample is reanalyzed. When reanalysis is indicated, the data for each parameter are examined for possible analytical error. Any suspect parameters are then reanalyzed and the above percent differences recalculated.

Table 4. Conductance Factors (F) of Ions

Ion[a]	Conductance (μS/cm at 25°C) per μeq/L	Ion[a]	Conductance (μS/cm at 25°C) per μeq/L
Ca^{2+}	0.052	NO_3^-	0.071
Mg^{2+}	0.047	Cl^-	0.076
Na^+	0.049	SO_4^{2-}	0.074
K^+	0.072	HCO_3^-	0.044
H^+	0.350	OH^-	0.198
NH_4^+	0.075		

[a] H^+ and OH^- calculated as: $[H^+] = 10\text{–pH} \times 10^6$ μeq/L.

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APPENDIX B

LABORATORY NOTEBOOK GUIDELINES
ENVIRONMENTAL RESEARCH LABORATORY - CORVALLIS
RESEARCH NOTEBOOK GUIDANCE

1. ERL-C staff should use bound pre-numbered laboratory and field notebooks. If it is necessary to use loose data sheets, the sheets should be consecutively numbered and bound before storage in the archive.

2. Notebooks with carbon-copy pages are recommended. It is recognized that carbon-copy notebooks are not suitable for use by all laboratory staff. A notebook system that is appropriate for staff use should be determined in consultation with quality assurance (QA) staff. Non-carbon notebooks are to be photocopied and stored in a location different from the storage area of the orginial notebook. Carbon copies should be bound and stored in a location different from the original notebook.

3. Archive storage procedures for laboratory notebooks should be determined by the project officer at the beginning of the project and managed within each project. The length of time archive records should be retained and the location of archive storage should be defined in the project's quality assurance project plan (QAPP).

4. Notebook entries should be made in ink and each entry dated. Mistakes should be crossed out with a single line and initialed. Exceptions to this rule will be determined by the project officer and will be made with the agreement of the QA staff.

5. Spaces and pages left blank should be crossed out to prevent entries from being made at a later time. Dates of entry should be provided on each page.

6. Project staff working in a shared notebook should initial and date each entry. The full name and initials of each person sharing the notebook should appear at the beginning of the notebook. Persons with the same initials should determine a convention to differentiate between entries.

7. Pages should not be removed from any notebook.

8. Supporting records can be included in the laboratory notebook. These records should be attached with glue, staples, or tape. Attached records should be signed and dated to overlay both the page and the record so that removed records can be identified.

9. Supporting results and conclusions (e.g., computer printouts, data sheets, calibration records) should be referenced in sufficient detail to allow retrieval of the record.

PART II:
LONG-TERM MONITORING PROJECT
DATA DICTIONARY

December 1991

By

Avis D. Newell
Randy Hjort
ManTech Environmental Technology, Inc.
c/o U.S. EPA Environmental Research Laboratory
200 S.W. 35th Street
Corvallis, OR 97333

SECTION 1
INTRODUCTION

1.1 INTRODUCTION

This document is a guide for data users of the United States Environmental Protection Agency's (EPA) Long-Term Monitoring (LTM) Project data base. This dictionary describes the data base, lists and defines the variables included in the data base, and briefly describes the LTM Project.

The LTM Project was intended to measure chemical trends in surface waters of the United States expected to be susceptible to acidification from acidic deposition (see Section 2 of this document, Newell et al., 1987; Newell, in press). The lakes and streams were chosen in clusters, across sulfate and hydrogen ion depositional gradients, in different geographic regions of the United States. Sites for which data already existed were chosen preferentially, in an effort to extend the period of record for the program. Water chemistry and limited hydrologic data are collected at the LTM sites. These data comprise the data base described here.

1.2 DATA DICTIONARY DESCRIPTION

This document is organized to suit two purposes: (1) to provide background information about the project and the data set for the user, and (2) to concentrate specific information about the variables in the data set in easily accessed sections for quick reference. Changes in the methods used to collect the data, and the resulting data substitutions, may affect interpretation of the data. Thus the data user is strongly urged to read this report carefully before using the data.

Section 2 provides background information about the LTM Project, including information about the cooperators who participate in the project and the numbers of lakes and streams included in the data set. The remainder of the document describes the structure of the LTM data base and provides information pertaining to the use of the data. The project guidelines for data quality are outlined in Section 3. In order to identify as many erroneous data as possible, both the individual cooperators and the EPA have validated the data. The procedures followed in this process are described in Section 3, followed by a description of the data substitutions made and the tags assigned to the data as a result of the validation process. Section 4 contains information about the data base itself, including a description of the structure of the data set, the variables

included, and definitions of the variables. Appendix A is a list of the sites included in the data set; Appendix B lists the period of record for each variable in each region. The QA Plan, describing the procedures used in the LTM Project and the requirements for data quality, is included as Part I of this publication.

SECTION 2
PROJECT DESCRIPTION

The LTM Project was initiated by the EPA in 1983, under the National Acid Precipitation Assessment Program (NAPAP). A committee of representatives from several federal agencies produced a protocol for the project. Sampling was initiated in the fall of 1983, with personnel from state and federal agencies and universities cooperating to complete the sampling and chemical analyses (Table 2-1). Although the data are now available to the public, the LTM cooperators have requested that researchers using this data base contact the cooperator who collected the data of interest. A contact person and respective address for each region are included in Table 2-1. In addition to the professional courtesy extended, contact with the investigators most familiar with the sites and data will yield valuable information to any one interested in the LTM data.

Surface waters in several regions of the country are included in the LTM project (Figure 2-1):

- 5 Tunk Mountain watershed Lakes in Maine
- 24 lakes throughout the state of Vermont
- 16 lakes in the Adirondack region of New York
- 28 lakes in the Upper Midwest (UMW), including northeastern Minnesota (4 lakes), northcentral Wisconsin (13 lakes), and the Upper Peninsula of Michigan (11 lakes)
- 10 lakes in the Mt. Zirkel (4 lakes) and Weminuche (6 lakes) Wilderness areas of Colorado
- 7 streams in the Catskill region of New York

In four other regions, sampling was conducted briefly and then discontinued--lakes in Montana and the Southern Blue Ridge region of the southeast, and streams in Pennsylvania and the Sand Hills of North Carolina. The period of record is too short, however, for data from these regions to be included in the data base. More details about the lakes monitored and the methods used can be found in Newell et al. (1987) and in the QA plan included in this volume.

Although LTM funding was not available until the fall of 1983, prior data were available for many of the lakes monitored in the LTM Project, from monitoring programs already established in

TABLE 2-1. EPA'S LONG-TERM MONITORING (LTM) PROJECT[a]

Location	Contact Person	Affiliation	Number of sites	Beginning of Record	Sampling Schedule
Adirondacks,[b] New York	Charles Driscoll	Dept. Civil & Environ. Eng. Syracuse University Syracuse, NY 13244	16 lakes	Summer 1982	Monthly
Vermont	Doug Burnham	Vermont Department of Environmental Conservation 103 S. Main St. Waterbury, VT 05676	24 lakes	Winter 1981	Seasonal
Maine	Steve Kahl	Sawyer Environmental Center University of Maine Orono, ME 04469	5 lakes	Fall 1982	Spring, summer, fall
Upper Midwest[c]	Patrick Brezonik	Dept. Civil Eng. University of Minnesota Minneapolis, MN 55455			
Minnesota			4 lakes	Fall 1983	Spring, summer, fall
Wisconsin			13 lakes	Fall 1983	
Michigan			11 lakes	Fall 1983	
Rocky Mountains, Colorado	John Turk	U.S. Geological Survey Bldg. 53, Mail Stop 415 Denver Federal Center Lakewood, CO 80225	10 lakes	Summer 1985	Monthly in summer
Catskills, New York	Pete Murdoch	U.S. Geological Survey Water Resources Division Box 744 Albany, NY 12201	7 streams	Fall 1983	9 times per year

[a] Although similar tables exist in other publications, the information provided here reflects information included in the LTM data base.

[b] Three years of data collected for most of these lakes between 1982 and 1985 by Syracuse University were funded by the Electric Power Research Institute during the Regional Integrated Lake Watershed Acidification Study (Driscoll, pers. comm); these data are included in the LTM data base.

[c] Data collected by the University of Minnesota at Duluth through a cooperative agreement with the EPA Environmental Research Laboratory, Duluth, are available for most of these lakes for the period 1978-1982 (Glass, pers. comm).

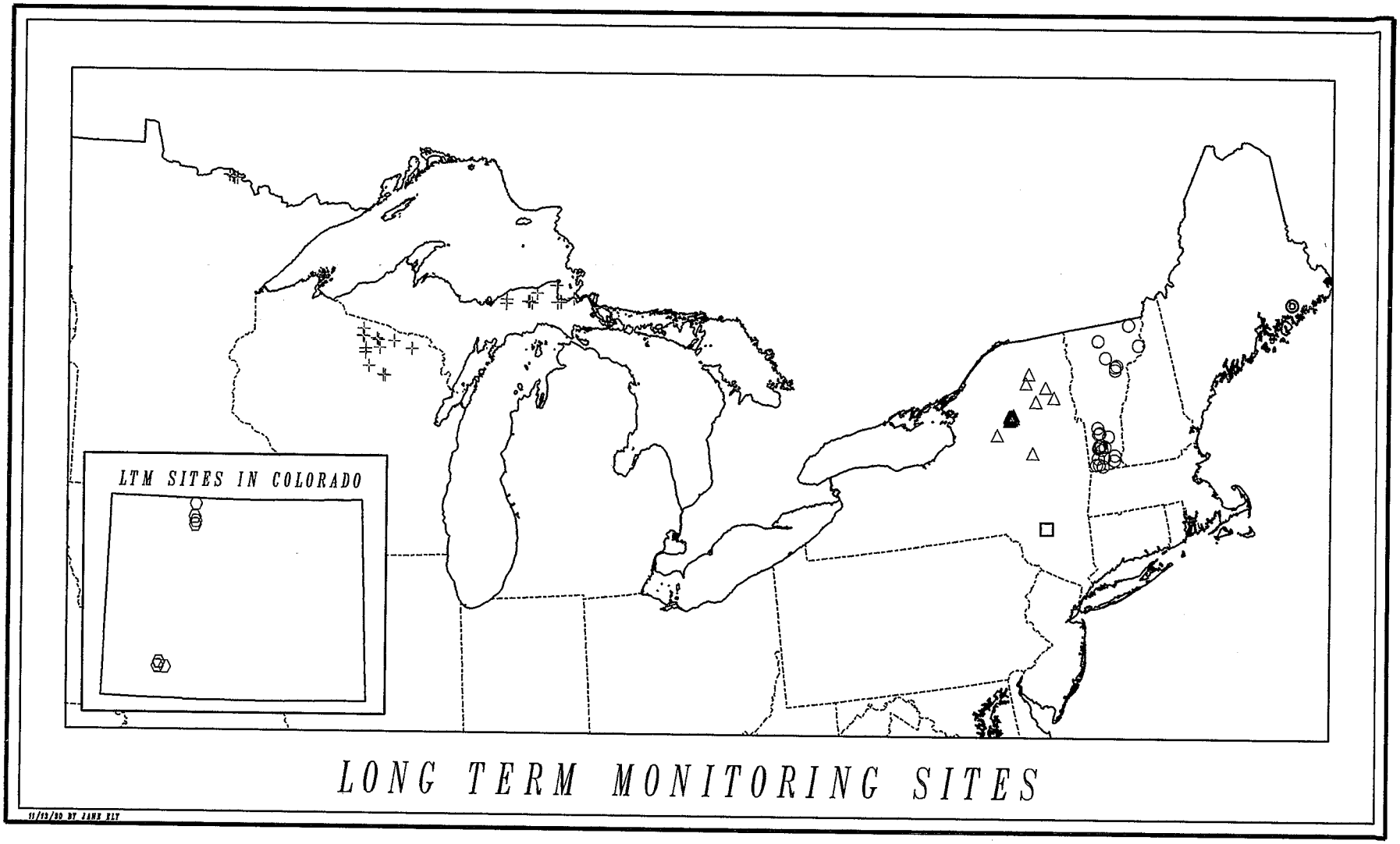

Figure 2-1. **Map showing the locations of EPA Long-Term Monitoring sites. Octagons represent the Colorado lake sites; crosses show the Upper Midwest lakes; triangles depict Adirondack lakes; the single square represents seven Catskill streams; thin-lined circles show Vermont lake locations; the bullseye depicts the five Maine lakes.**

most of the regions. The EPA funded monitoring in Vermont beginning in 1980, and data that had been collected for a year and a half for lakes in Maine were already available. LTM funding for the Adirondack region was initiated in the spring of 1985, but three years of previous sampling in those lakes had been sponsored by the Electric Power Research Institute (EPRI), as part of the Regional Integrated Lake Watershed Acidification Study (RILWAS; Driscoll, pers. comm). For these three projects, continuity among investigators, laboratories, and methods was maintained throughout the funding changeover, so the entire period of record is included in this data base.

Data for the Upper Midwest were collected as early as 1978. From 1978 through the summer of 1983, data were obtained by Gary Glass at the EPA laboratory in Duluth. Continuity of laboratories and sampling methodology was not maintained during this funding changeover, thus there may be unquantified step changes in variable values beginning with data for the fall of 1983. Therefore, the earlier Upper Midwest data (1978–1983) have not been included in the LTM data base.

As a result of the cooperative effort, LTM samples have been analyzed by laboratories associated with the cooperators in each region. Due to the inclusion of pre-existing sites, project guidelines followed rather than preceded initial data collection. Collection and analytical methods thus vary across regions, so it is difficult to make direct comparisons of data from one region to another. Analytical and sampling method changes through time within each region resulted from incorporation of the overall project guidelines and are described in Section 4.

Required variables measured by the LTM cooperators are acid neutralizing capacity (ANC), pH, specific conductance, dissolved cations (Ca, Mg, Na, K, total Al), dissolved anions (SO_4^{2-}, NO_3^-, Cl^-), true color, and temperature. Other variables measured by some cooperators include dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), F^-, and various species of Al, and N. Section 5 contains a complete listing, with definitions, of lake and stream variables.

Lake sites in Vermont are sampled once during each season of the year, whereas lake sites in the Upper Midwest and Maine are sampled during three seasons, excluding winter. Colorado lakes are also sampled three times during the ice-free season, typically July through September. At the high elevations of these sites, this period corresponds roughly to the spring, summer, and fall sampling period in Maine and the Upper Midwest. Adirondack data were collected monthly during the RILWAS project; this schedule was maintained when the sites were funded by LTM. In the Catskill stream monitoring program, monitoring was conducted nine times per year, under

both high- and low-flow conditions. The EPA-funded Episodic Response Project (1988-1990) included some of the LTM Catskill stream sites. This project entailed episodic sampling during storm or meltwater events. Episodic data collected at these LTM Catskill stream sites are not included in the LTM data base, but will be available in the Episodic Response Project data base (Wigington, pers. comm.).

The lake and stream data bases differ slightly to accommodate the different variables appropriate to the lake and stream sites. For consistency, all of the lake data sets contain the same variables, despite the fact that some regions do not measure every variable.

Deposition data are not measured as part of the LTM project. Several monitoring networks, including the National Acid Deposition Project/National Trends Network (NADP/NTN), the Utility Acid Precipitation Study Program (UAPSP), Acidic Precipitation in Ontario Study (APIOS), and Canadian Acid Precipitation Monitoring Network (CAPMoN), provide the deposition information for the LTM regions (Watson and Olsen, 1984).

SECTION 3
DATA BASE QUALITY

3.1 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) OF LTM DATA

Data quality objectives have been developed for the LTM Project, and can be expressed in terms of quality assurance (QA) objectives for precision, accuracy, and detection limits. LTM cooperators are required to meet the QA objectives listed in Table 3-1, so these objectives can be used as a general indication of data quality in the LTM data base. The LTM QA plan, Part I of this publication, defines these data quality indicators and describes in detail the procedures for sample collection, analysis, and quality control (QC) that are used to meet these objectives.

Analytical detection limits are monitored in LTM laboratories as a check on analytical performance and consistency. For example, drifting detection limits may indicate the need for equipment maintenance. Detection limits are calculated as three times the standard deviation of replicate analyses of a low-level standard or QC check sample (Taylor, 1987).

The precision requirements listed in Table 3-1 refer to within-batch analytical precision. Precision is calculated as percent relative standard deviation (%RSD), the standard deviation of replicate values divided by the mean, times 100. LTM cooperators are also required to collect field duplicate samples in order to estimate sampling precision. The field duplicates are averaged in this final data set.

The accuracy requirements listed in Table 3-1 are expressed as the percent difference from a certified reference sample, audit sample, or QC check sample. In addition to accuracy, bias in the LTM laboratories has been estimated, beginning in 1988, through participation in the Long Range Transport of Airborne Pollutants (LRTAP) Interlaboratory Comparability Studies (Aspila, 1989). Bias is a systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system (Taylor, 1987). The LRTAP studies send 10 natural water samples to over 40 participating laboratories in North America during each study. A ranking procedure is used to identify and describe bias. If bias is identified for a variable in an LTM laboratory, then probable causes of the bias are investigated in order to correct the bias.

LTM cooperators are responsible for tracking the quality of their data. A standard QA plan was not in place when the LTM projects began. Rather, LTM cooperators submitted separate

TABLE 3-1. QUALITY ASSURANCE OBJECTIVES: REQUIRED ANALYTICAL DETECTION LIMITS, WITHIN-LABORATORY RELATIVE PRECISION, AND ACCURACY OBJECTIVES

Variable	Reporting Units	Required Detection Limit	Intralab Relative Precision (%)[a]	Accuracy (%)[b]
Required measurements				
pH, field	pH units	--	± 0.1 pH unit	--
ANC	μeq/L	--	± 5 μeq/L if ANC ≤ 30 10% if ANC > 30	10
Conductivity	μS/cm	--[c]	± 2 μS/cm if cond. ≤ 25 5% if cond. > 25	5
Color	Pt-Co units	0	± 5 Pt-Co units	--
SO_4^{2-}	μeq/L	1.0	5	10
NO_3^-	μeq/L	0.1	± 2 μeq/L if NO_3 < 15 10% if NO_3 ≥ 15	10
Cl^-	μeq/L	0.3	5	10
Ca	μeq/L	0.5	5	10
Mg	μeq/L	0.8	5	10
Na	μeq/L	0.4	5	10
K	μeq/L	0.3	5	10
Al, total dissolved	μg/L	5	20 if Al ≤ 50 μg/L 10 if Al > 50 μg/L	20 if Al ≤ 50 μg/L 10 if Al > 50 μg/L
Additional measurements				
DIC	mg/L	0.05	10	10
DOC	mg/L	0.1	10 if DOC ≤ 5 mg/L 5 if DOC > 5 mg/L	10
F^-	μeq/L	0.3	5	10
NH_4^+	μeq/L	0.6	5	10
SiO_2	mg/L	0.05	5	10

[a] Expressed as percent relative standard deviation (standard deviation divided by the mean) when concentrations measure at least 10 times above instrumental detection limits, unless concentration range is noted, or if ± units appear, as plus or minus the specified number of units.

[b] Expressed as percent difference from a reference value.

[c] Blank must be < 2.0 μS/cm.

plans for approval. Since then, an overall QA plan has been adopted that allows for procedural flexibility among regions. Each region has specified criteria for data validation checks, such as ion balances and conductance ratios, which are listed in the LTM QA plan. Each cooperator is responsible for ensuring that these criteria are met, with annual EPA review of the required QA data.

3.2 DATA VALIDATION

Spurious contamination, analytical errors, and reporting errors can lead to incorrect data values that do not reflect the natural variation of the surface water represented and that can affect statistical analyses and interpretation. Many of these errors can be identified through careful examination of the data. This examination, termed data validation, is a process of checking for internal consistency among the data values. Ion balances, intervariable relationships, and comparison to other data collected at the same sites leads to identification of questionable data values (Section 3.2.1). In this data base, data values clearly in error have been removed. Each analytical variable in the data set has an affiliated tag variable, and the value of the tag variable indicates whether the datum has been removed as a result of the validation process (Section 3.2.2) or replaced.

3.2.1 Outlier Identification

Strong relationships among variables can be examined to identify data points that are in error. Table 3-2 lists the several types of relationships that are inspected. Scatter diagrams can be used to identify outliers, despite the lack of a linear relationship, by identifying points that are far away from the majority of points. Linear regression can be used to quantitatively identify outlying data points of linear relationships by examining those points that lie more than 2.5 times the studentized residuals from the predicted values. Outliers on the histograms of ion ratios and ion differences are those that occur at values beyond the acceptable values for those variables, as defined in the LTM QA plan.

Univariate distributions of the data from each lake over time are also inspected for outliers. Many of the chemical data do not follow a normal distribution, thus not all "outliers" identified in comparing the data to normality are in error. However, inspection of these distributions can help to identify the variable in error in a bivariate relationship, and can suggest further investigation of data, such as SiO_2 or Al, for which there are not good binomial relationships.

TABLE 3-2. RELATIONSHIPS USED IN DATA VALIDATION PROCEDURES

Scatter diagrams

- pH vs. ANC
- Anion deficit vs. DOC
- Anion deficit vs. organic ion

Potentially linear relationships[a]

- Mg vs. Cl^-
- Mg vs. SO_4^{2-}
- Na vs. Cl^-
- Na vs. SO_4^{2-}
- Ca vs. Cl^-
- Ca vs. SO_4^{2-}

Generally linear relationships

- ANC vs. Ca
- ANC vs. Ca + Mg
- Mg vs. Ca
- Calculated (Kanciruk, 1985) vs. measured conductance
- Sum of cations vs. organic ion + sum of anions

Histograms for inspection

- Ratio of sum of anions : sum of cations
- Ion difference (sum of anions — sum of cations)

Box and whisker diagrams

- Each chemical variable across all lakes, by each sampling event
- Each chemical variable across all sampling events for each lake

[a] These are often not linear when one variable has a small range of concentrations across all lakes within a region, as commonly occurs for Cl^- at sites distant from the coast.

The procedure developed for identifying questionable data values was as follows. Plots of the relationships listed in Table 3-2 were inspected. For linear relationships, data values outside of 2.5 studentized residuals from the regression were listed in a data file. Outliers for histograms and nonlinear relationships were identified by eye, and also included in the outlier data file. Comment fields in this data file indicated which relationship led to the identification of the questionable data point. Sorting the list by observation number allowed data points that were outliers in more than one relationship to be identified. Each of these observations was examined to determine which if any of the variables should be tagged. Grouping the data as described facilitated this effort. The list of outliers was then compared to plots of the data over time, to see if all suspicious data had been identified. The final list of suspicious data was sent to each cooperator for inspection with resultant confirmation or correction of erroneous data.

Several of the suspicious points were caused by analytical problems, and these were tagged and excluded from trend analysis (see Section 4). Others resulted from sampling conditions, such as sampling under ice or just after a storm, and they were maintained in the data set. The distinction between analytical and sampling influences was made by the cooperator who collected the data. Thus, it is imperative to have cooperator input in assigning tags. Deleting correct data from analyses can have as large an impact on interpretation as including poor data, because the deletion can greatly affect the variance estimates.

3.2.2 Tag Assignments

Tag variables have been created for each of the variables that require measurement in the data sets. Tags are assigned to each variable as appropriate, resulting from validation, substitution, or analysis. The values assigned to the tag variables, called tags, provide information about the data sources. A list of possible tag values and their meanings appears in Table 3-3. Three tag values appear in the final data set: 'X,' 'S,' and 'Z'. Values that were clearly in error, but for which no corrective action could be taken, were replaced with missing values in the final data set, and tagged with an 'X', to indicate that original data existed but were not acceptable.

The 'Z' tag is used to indicate concentrations that are below the detection limit for a particular variable. These observations have a value of zero in the data set, in order to standardize data that are below the detection limit in the LTM data base. The values reported to the U.S. EPA Environmental Research Laboratory in Corvallis (ERL-C) for these variables ranged

TABLE 3-3. TAG VALUES FOR CHEMICAL VARIABLES IN THE LTM DATA BASE

S	This is a substituted value (see Sections 3.2.2, 4)
X	This missing value resulted from exclusion of poor data
Z	This zero value resulted from a below detection limit response

from zero to the detection limit value, but were censored data; the analytical reading was reported as either the detection limit value or as zero before the data were submitted to the EPA. The standard "below detection limit" value chosen for this LTM data base was zero. As a result of reporting low-level data in this way, the only negative values in the data set are for ANC, a variable that commonly has negative values in acidic lakes.

A complete list, including definitions, for the data base variables is included in Section 5. However, in an attempt to reconcile method changes occuring throughout the period of record, some data values have been replaced with values collected by methods that differ from those described in the variable definitions. These substitutions may or may not have required a calibration process; they are described in Section 4 for each region.

The tag value of 'S' identifies data where substitutions were made. Substitutions made in each region (described in Section 4.1) were based on studies where both methods were compared for a single set of samples for each region (Newell and Morrison, in press). By far, the most common substitution was to use unfiltered data as estimates of the filtered value, in the manner indicated by the appropriate overlap study. For most of these observations, no values were changed; the 'S' is present to indicate that the data were collected under different protocols. Other method changes included the anion analysis method and the sample collection procedure used in Vermont. These more commonly required calibration of the data during the substitution process. These substitutions are briefly described in Section 4.1, and are described in greater detail in Newell and Morrison (in press).

SECTION 4
REGIONAL DATA CHARACTERISTICS

This section provides information on some of the individual characteristics of each regional data set. Not all chemical variables are measured by each cooperator. Other differences, such as sample collection method and sampling schedules, occur among cooperators. This section briefly summarizes the method changes that have occurred in each region and how these changes were dealt with in the data base, which should be considered in interpretation of the data set.

4.1 MAINE DATA CHARACTERISTICS

Maine lakes have been monitored since 1982. Samples are taken in spring, summer, and fall for these lakes. Variables not measured in the Maine lakes include monomeric and organic Al, DIC, F^-, NH_4^+, and Si.

Samples were unfiltered prior to the spring of 1983. Anion data have always been analyzed by ion chromatography (IC), which has an associated prefilter. However, from spring 1983 on, all anion samples were first filtered through a 0.4-μm polycarbonate filter. We presumed that due to the IC prefilter, there would not be significant differences between filtered and unfiltered anions, although we do not have data from an overlap study to confirm this. Overlap data do exist for filtered and unfiltered cation data in these Maine lakes; they indicate that filtration has not had a significant effect on the measurement of major cation concentrations: Ca, Mg, Na, and K. Thus for the anions NO_3^-, SO_4^{2-}, and Cl^-, and the cations Ca, Mg, Na, and K, unfiltered data prior to spring 1983 have been included in the data set under filtered variable names and accompanied with a substitution tag. There was a significant filtration effect on total Al concentration; therefore, Al data prior to the spring of 1983 were not included in this data set.

The meter used to measure specific conductance from the project inception through the fall of 1983 was found to be faulty, and was replaced prior to spring 1984 sampling. These early data were considered to be unreliable, and are not included in the data set. The missing conductance values are accompanied by an 'X' tag.

In the summer of 1985, the method of measuring pH in these Maine lakes was changed to the closed cell method used during the National Surface Water Surveys (NSWS; U.S. EPA, 1989). Thus pH values prior to this date were not included in the data set.

4.2 VERMONT DATA CHARACTERISTICS

Data have been collected from Vermont lakes since 1980. Samples are taken seasonally, winter, spring, summer and fall. At the project inception, some lakes were monitored in alternate years, thus there is not a complete annual record for every lake. Variables not measured in the Vermont sampling program are monomeric or organic Al, DIC, DOC, F^-, NH_4^+, Si, or SiO_2.

Early ANC values were not measured using the Gran titration method, so ANC values are commonly missing in 1980 and 1981; only Gran ANC values are included in the data base. Not all cations and anions were measured during the first two years. Samples from the inception of the project through the summer of 1984 were not filtered. Studies on filtered and unfiltered split samples indicated that filtration affected only the analyses for Ca and Na. The Ca and Na unfiltered values were calibrated (Newell and Morrison, in press), whereas the remaining unfiltered cation values, Mg and K, were substituted into the data set without applying a calibration equation.

Anion methods were changed from colorimetric to ion chromatography after the spring sample in 1985. Overlap studies for SO_4^{2-} and Cl^- provided calibration curves to account for both the analytical method change and the filtration change concurrently (Newell and Morrison, in press). These anion value tags have been assigned an 'S' value, indicating that the value in the data base is a substitute value. Nitrate was not calibrated, nor were early colorimetric values included in the data base, as the colorimetric data were total $NO_3^- + NO_2^-$, and the IC data reflected dissolved NO_3^- concentrations only.

Sample collection methods were also changed in Vermont in early 1985. Early in the project, a hose sampling method was used to collect integrated-column samples. A 6-m hose was lowered into the lake, collecting a vertical column of water. In unstratified lakes, hose sampling probably mimics epilimnetic sampling reasonably well. However, the full 6 m of hose was filled with sample, regardless of the stratification status of the lake. Thus, for the deeper lakes, summer samples occasionally contained hypolimnetic water. This sampling method was changed to use of a Kemmerer sampler during early 1985. In this method, a discrete epilimnetic

sample was taken at 1 m depth, and an additional Kemmerer sample was taken at 1 m above the lake bottom only when the lake was stratified. Overlapping samples, using both methods at the same site at the same time, indicated that a bias existed between the two methods, regardless of stratification status (Newell and Morrison, in press). The bias was found to be significant for ANC, pH, Ca, and SO_4^{2-}. The hose values for these variables were calibrated according to the equations described in Newell and Morrison (in press). As all data were calibrated to reflect Kemmerer epilimnetic samples, the SAMSTRAT variable was given a value of 'EPI.'

4.3 ADIRONDACK DATA CHARACTERISTICS

This data set includes data funded by the EPA (INVEST='LTM') and data funded by EPRI as part of RILWAS (INVEST='RILWAS'). No method changes occurred in the Adirondack data set, so tag values reflect either spurious analytical problems ('X') or data below detection limit ('Z'). Samples are taken monthly, although some lakes have been sampled biweekly during spring runoff. Most lakes are sampled at the lake outlet, with the exception of Little Echo Pond (LAKEID 1A1-107), a seepage lake with no outlet present. Variables not measured in the Adirondack program are total filtered Al and true color.

4.4 UPPER MIDWEST DATA CHARACTERISTICS

Data have been collected seasonally from many of the Upper Midwest lakes since 1978. From 1978 until 1983, the data were collected by Gary Glass at the EPA Environmental Research Laboratory in Duluth, Minnesota (pers. comm.). Analytical and filtration procedures changed significantly between this and the LTM project, without comparative overlap studies to quantify the effect of the changes. Thus, the earlier data have not been included in this data base.

Twenty-eight lakes have been monitored seasonally, except in winter, in three Upper Midwest states: Minnesota, Wisconsin, and Michigan's Upper Peninsula. Samples are taken from the deepest part of the lake, at a depth of 1 m, with an additional hypolimnetic sample collected at 1 m above the bottom when a lake is stratified. Monomeric and organic Al, DIC, and Si are not measured in this LTM project.

Beginning in fall of 1983, aliquots for anions and cations were prepared separately, and filtered through different filters. Anions were filtered through 0.45-μm cellulose triacetate filters for the fall 1983 sample. In the spring of 1984, these filters were changed to 0.4-μm polycarbonate

filters. This filter change appeared to have an effect on low concentrations of Cl^- and NO_3^-. Thus fall 1983 Cl^- and NO_3^- values have been removed from the data base and tagged with an 'X'.

Cation aliquots were filtered through glass fiber prefilters and 0.1-μm polycarbonate filters until summer of 1985 when the two-filter sequence was replaced with a single filtration through 0.4-μm polycarbonate filters. Overlap studies, and indeed mere data inspection, showed a significant filtration effect of the two-filter system on Na and K concentrations. This effect was too extreme and too variable for the data to be calibrated, thus these values have been removed from the data base, and tagged with an 'X'. The overlap studies indicated no filtration effects on Ca or Mg data.

The DOC analytical procedure used in the fall of 1983 was found to be unreliable. It was modified for the spring 1984 sample analyses. The fall 1983 values are also excluded from the data set and tagged accordingly.

4.5 COLORADO DATA CHARACTERISTICS

Ten lakes in two wilderness areas of Colorado have been monitored since the summer of 1985. The sampling schedule of these high-elevation lakes (> 3,000 m) differs from the other regions due to the very long winter season of the mountainous location. Samples are taken shortly after ice-out in July, during midsummer in August, and before ice cover in September. Epilimnetic and hypolimnetic Kemmerer sampling is used in four of the Colorado lakes: Elbert, Seven, Eldorado, and Little Eldorado. Outlet sampling is performed at the remaining sites. The sampling method is indicated in the value of SAMSTRAT, where EPI reflects epilimnetic sampling, and OUT refers to outlet sampling. Variables not measured in the Colorado lakes are monomeric and organic Al and SiO_2. The LTM data base contains only the routine samples.

4.6 CATSKILL STREAM DATA CHARACTERISTICS

Funding for Catskill stream monitoring was initiated in 1983. By 1986, another EPA project, the Episodic Response Project, also funded episodic sampling for three of the same sites. The Episodic Response Project data base (Wigington, pers. comm.) will contain the episodic data for two LTM streams, the East Branch of the Neversink, at both the headwater and mid-length reaches, and High Falls Brook. Variables not measured in the Catskill Stream data set include

monomeric and organic Al, color, DIC, F^-, NH_4^+, and Si. Streams are sampled nine times per year, independent of flow conditions.

Filtration changes have occurred during the period of record for Catskill streams. The available overlap data do not indicate significant filtration effects in these streams, but not all overlap data sets are large enough to conclude that no differences exist due to filter changes. Polycarbonate 0.1-μm filters were used from the project initiation until August 1988; thereafter aliquots for all major cations and anions were filtered through 0.4-μm polycarbonate filters (Newell and Morrison, in press). These filters were used until August 1989, when they were replaced with 0.45-μm cellulose ester filters (Newell and Morrison, in press). Polycarbonate (0.1 μm) filters were used to filter the Al aliquots until August 1989. After this time, 0.2-μm cellulose ester filters were used.

SECTION 5
DATA BASE DESCRIPTION

5.1 SAS DATA BASE

The LTM data are contained in a SAS (SAS, 1985) data base, often referred to as a library, with separate files for each LTM region. The data base, with member data sets, is described in Table 5-1. The SAS system easily lends itself to statistical analyses, and has extensive graphics capabilities. The LTM data base was created from data sets in various formats. SAS data sets were provided by the Wisconsin Department of Natural Resources (WDNR). Data from other regions were provided in either ASCII (Maine, Vermont and Colorado lake data) or LOTUS files (Adirondack data).

The available variables differ somewhat among regions, but the variable lists for all lake data sets are similar. The variables included in the stream data set differ somewhat from those for the lakes. Each observation in the data set has a unique identifier (MERGEID), built from the lake or stream ID, to facilitate correct merges.

Each record in the data set represents a separate analysis of water. Multiple observations per day at each site may result from samples collected at various depths, or at various times during a storm in the Catskill streams. Collocated duplicate samples have been averaged for this data set. The variables and their SAS attributes are listed in Table 5-2 for the lake and stream files. These variables are defined in detail in alphabetical order in Table 5-3. A list of LTM sites and locations is presented in Appendix A, and the period of record for each variable for lakes and streams in each region is listed in Appendix B.

5.2 VARIABLE DEFINITIONS

Table 5-3 contains detailed definitions for each variable. A short description of the analytical methods or the source of the data is included in the definition. Analytical methods are described in greater detail in the QA plan, Part I of this publication.

Physical variables, such as watershed and lake area and elevation, were obtained from the National Surface Water Survey data base (Kanciruk et. al., 1986, 1987). Most of the LTM lakes were sampled as part of these surveys (Linthurst et al., 1986; Landers et al., 1987). Some of the Catskill stream sites were also included in the National Stream Survey (Kaufmann et al., 1988). Data for sites not included in these surveys were obtained from individual cooperators.

TABLE 5-1. NAMES AND ATTRIBUTES OF THE DATA SETS INCLUDED IN THE LTM DATA BASE

Region	Data Set Name	# Obs	# Variables	# Bytes
Maine	MEDS4	122	62	68,154
Vermont	VTDS4	843	63	430,817
Adirondacks	ADDS4	1,567	62	794,989
Catskills	CATDS4	431	60	228,972
Upper Midwest	UMWDS4	526	62	271,366
Colorado	CODS4	165	62	89,783

TABLE 5-2. VARIABLES INCLUDED IN THE LAKE AND STREAM DATA SETS[a]

Variable	Type	Length	Format	Label
ALFIL	N	8	F8.1	Total filtered Al, μg/L
ALFILT	C	8		Total filtered Al tag
ALMON	N	8	F8.1	Monomeric Al, μg/L
ALMONT	C	8		Monomeric Al tag
ALORG	N	8	F8.1	Organic Al, μg/L
ALORGT	C	8		Organic Al tag
ANC	N	8	F8.1	ANC, Acid Neutralizing Capacity, μeq/L
ANCT	C	8		ANC tag
CAFIL	N	8	F8.1	Calcium, filtered, μeq/L
CAFILT	C	8		Calcium, filtered, tag
CLFIL	N	8	F8.1	Chloride, filtered, μeq/L
CLFILT	C	8		Chloride, filtered, tag
COLTRU	N	8	F8.0	True color (PCU)
COLTRUT	C	8		True color (PCU) tag
COND	N	8		Conductance, μS/cm
CONDT	C	8		Conductance tag
DATSMP	N	8	DATE7.	Date sampled, ddmmmyy (i.e., 07NOV80)
DIC	N	8	F8.2	Dissolved inorganic carbon, mg/L
DICT	C	8		Dissolved inorganic carbon tag
DOC	N	8	F8.1	Dissolved organic carbon, mg/L
DOCT	C	8		Dissolved organic carbon tag
ELEV	N	8	F8.1	Lake/stream elevation
FFIL	N	8	F8.1	Fluoride, filtered, μeq/L
FFILT	C	8		Fluoride, filtered, tag
FLOW#	N	8	F8.5	Stream discharge, m^3/s
FLOWT#	C	8		Flow tag
HYDROTYP*	C	8		Lake hydrologic type (drainage, seepage, etc.)
INVEST	C	8		Investigator

[a] This table includes the names of all variables in alphabetical order. The variable name is under VARIABLE and a short definition of the variable appears under LABEL. TYPE refers to character (C) or numeric (N) values. The length of the variable appears under LENGTH and the SAS format is in the FORMAT column. # = stream data set only; * = lake data set only.

(Continued)

TABLE 5-2. VARIABLES INCLUDED IN THE LAKE AND STREAM DATA SETS[a] (Continued)

Variable	Type	Length	Format	Label
KFIL	N	8	F8.1	Potassium, filtered, μeq/L
KFILT	C	8		Potassium, filtered, tag
LAKEID*	C	10		NSWS lake identification
LAKENAME*	C	30		Lake name
LAKESIZE*	N	8	F8.1	Lake surface area, ha
LATDD	N	8	F8.4	Lake latitude, decimal degrees
LONGDD	N	8	F8.4	Lake longitude, decimal degrees
MERGEID	C	15		Unique ID number for each observation
MGFIL	N	8	F8.1	Magnesium, filtered, μeq/L
MGFILT	C	8		Magnesium, filtered, tag
MONTH	N	2	F2.0	Month sampled, 1-12
NAFIL	N	8	F8.1	Sodium, filtered, μeq/L
NAFILT	C	8		Sodium, filtered, tag
NH4FIL	N	8	F8.1	Ammonium, filtered, μeq/L
NH4FILT	C	8		Ammonium, filtered, tag
NO3FIL	N	8	F8.1	Nitrate, filtered, μeq/L
NO3FILT	C	8		Nitrate, filtered, tag
ORGION	N	8		Estimated organic ion, (Oliver model)
PH	N	8		pH
PHT	C	8		pH tag
RT*	N	8		Retention time in years
SAMDP*	N	8		Sample depth, m
SAMSTRAT*	C	4		Stratum sampled (epi, hypo, etc.)
SAMTYP#	C	4		Sample type, baseflow (B), or episodic (E)
SEASON	C	1		Season sample taken (W, P, U, F)
SECCHI*	N	8		Secchi depth, m
SIFIL	N	8		Silicon, filtered mg/L
SIFILT	C	8		Silicon tag

[a] This table includes the names of all variables in alphabetical order. The variable name is under VARIABLE and a short definition of the variable appears under LABEL. TYPE refers to character (C) or numeric (N) values. The length of the variable appears under LENGTH and the SAS format is in the FORMAT column. # = stream data set only; * = lake data set only.

(Continued)

TABLE 5-2. VARIABLES INCLUDED IN THE LAKE AND STREAM FILES[a] (Continued)

Variable	Type	Length	Format	Label
SIO2	N	8	F8.2	Silica, filtered mg/L
SIO2T	C	8		Silica tag
SO4FIL	N	8	F8.1	Sulfate, filtered, μeq/L
SO4FILT	C	8		Sulfate, filtered, tag
STAGE*	N	8		Stage height in outlet stream, m
STATE	C	2		State of site location
STREAM#	C	8		Stream name
STREAMID#	C	10		Stream Id number
TIMSMP#	N	8	HHMM5.	Time sampled (2400 clock)
WSHED	N	8	F8.0	Watershed area, ha
WTEMP	N	8	F8.1	Water temperature, deg C
YEAR	N	4		Year sampled

[a] This table includes the names of all variables in alphabetical order. The variable name is under VARIABLE and a short definition of the variable appears under LABEL. TYPE refers to character (C) or numeric (N) values. The length of the variable appears under LENGTH and the SAS format is in the FORMAT column. # = stream data set only; * = lake data set only.

TABLE 5-3. VARIABLE DEFINITIONS AND REPORTING UNITS[a]

Variables	Units	Definition
ALFIL	μg/L	Total filtered aluminum. Graphite furnace atomic absorption (AAS).
ALFILT		Total filtered aluminum tag.
ALMON	μg/L	Monomeric aluminum. Hydroxyquinoline extraction into MIBK, graphite furnace AAS.
ALMONT		Monomeric aluminum tag.
ALORG	μg/L	Organic aluminum. Ion exchange column fractionation, hydroxyquinoline MIBK extraction, graphite furnace AAS.
ANC	μeq/L	Acid neutralizing capacity is a measure of the amount of acid necessary to neutralize the bicarbonate, carbonate, alurninohydroxy complexes, and other bases in a sample. Gran titration.
ANCT		ANC tag.
CAFIL	μeq/L	Filtered calcium. Atomic absorption spectrophotometry, with N_2O flame or La addition.
CAFILT		Filtered calcium tag.
CLFIL	μeq/L	Filtered chloride. Ion chromatography.
CLFILT		Filtered chloride tag.
COLTRU	PCU	True color. Visual comparator, filtered or centrifuged sample.
COLTRUT		True color tag.
DATSMP	Date7.	Date sampled (DDMMMYY, i.e., 07NOV80).
DIC	mg/L	Dissolved inorganic carbon. Gas chromatography.
DICT		Dissolved inorganic carbon tag.
DOC	mg/L	Dissolved organic carbon. Methods vary among cooperators.
DOCT		Dissolved organic carbon tag.
ELEV	meters	Elevation at which sampling site is situated.
FFIL	μeq/L	Filtered fluoride. Ion selective electrode, or ion chromatography.

[a] * = variable appears in lake data set; # = variable appears in stream data set only.

(Continued)

TABLE 5-3. VARIABLE DEFINITIONS AND REPORTING UNITS[a] (Continued)

Variables	Units	Definition
FFILT		Filtered fluoride tag.
FLOW#	cms	Stream discharge, measured in ungauged streams, calculated from stage:discharge relationships in gauged streams.
FLOWT#		Flow tag.
HYDROTYP*		Lake hydrologic type.
		DRAIN = Drainage: inlets and outlets present, or just outlets present. CLOSE = Closed lake: inlets but no outlets. SEEP = Seepage lake: no inlets and no outlets. RES = Reservoir: a lake with controlled flow.
INVEST		Principal investigator.
KFIL	μeq/L	Filtered potassium. Air-acetylene flame atomic absorption.
KFILT		Filtered potassium tag.
LAKEID*		A 7-character lake identification number from the National Surface Water Survey (Linthurst et al., 1986; Landers et al., 1987). The first character represents the region, the second character the subregion, the third character the alkalinity map class, and the last three digits the assigned lake number.
LAKENAME*		Lake name as identified by LTM cooperators.
LAKESIZE*	ha	Lake surface area, data from NSWS database.
LATDD NSWS	decimal degrees	Latitude expressed as decimal degrees in xx.xxxx format. From data base.
LONGDD	decimal degrees	Longitude expressed as decimal degrees in xxx.xxxx format. From NSWS data base.
MERGEID		Unique observation number for each observation. Assigned consecutively to file sorted by lake (LAKEID), date sampled (DATSMP), depth sampled (SAMDP), and sample type.
MGFIL	μeq/L	Filtered magnesium. Flame atomic absorption with N_2O flame or La addition.
MGFILT		Filtered magnesium tag.

[a] * = variable appears in lake data set; # = variable appears in stream data set only.

(Continued)

TABLE 5-3. VARIABLE DEFINITIONS AND REPORTING UNITS[a] (Continued)

Variables	Units	Definition
MONTH		Month sampled (1-12)
NAFIL	μeq/L	Filtered sodium. Air-acetylene flame atomic absorption.
NAFILT		Filtered sodium tag.
NH4FIL	μeq/L	Filtered ammonium.
NH4FILT		Filtered ammonium tag.
NO3FIL	μeq/L	Filtered nitrate. Ion chromatography.
NO3FILT		Filtered nitrate tag.
ORGION		Estimated organic ion concentration, from Oliver et al., 1983. Calculations: ORGION = (konst × DOC × 10)/(konst + 10^{-pH}), Where: konst = $10^{-(0.96 + 0.9 \times pH - 0.039 \times pH^2)}$.
RT*	Years	Retention time of water in lake. From NSWS data base. Calculated from lake and watershed area, site depth, and average precipitation and runoff.
SAMDP*	meters	Depth at which sample was taken.
SAMSTRAT*		Water stratum sampled: EPI = Epilimnion. OUTLET = Sampled in outlet of lake. HOSE = Epilimnetic sample taken with 6 m hose. KEMM = Epilimnetic sample taken at 1 m depth with Kemmerer sampler.
SAMTYP#		Type of stream sample. B = baseflow conditions
SEASON		Season when sample was taken: W = Winter. P = sPring. U = sUmmer. F = Fall.
SECCHI	meters	Secchi depth.
SIFIL	mg/L	Dissolved silicon. Measured by ICP on filtered samples.

[a] * = variable appears in lake data set; # = variable appears in stream data set only.

(Continued)

TABLE 5-3. VARIABLE DEFINITIONS AND REPORTING UNITS[a] (Continued)

Variables	Units	Definition
SIFILT	mg/L	Dissolved silicon tag.
SIO2	mg/L	Silica. Measured on filtered sample colorimetrically using molybdate or heteropoly blue.
SIO2T		Silica tag.
SO4FIL	μeq/L	Filtered sulfate. Ion chromatography.
SO4FILT		Filtered sulfate tag.
STAGE*	meters	Stage height from staff gauges in outlets.
STATE		State where site is located. (Two letter abbreviation).
STREAM#		Stream name, as used by LTM cooperator.
STREAMID#		WATSTORE ID code also used as stream ID in this data set.
TIMSMP		Time sampled, 2400 hour clock.
WSHED	ha	Watershed area of lake, from NSWS database.
WTEMP	°C	Water temperature at sample depth.
YEAR		Year of the date sampled.

[a] * = variable appears in lake data set; # = variable appears in stream data set only.

SECTION 6

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APPENDIX A

SITES INCLUDED IN THE LTM DATA BASE

This appendix lists the sites in each LTM region. The table includes the site name, the LTM-NSWS site identification number, the latitude and longitude of the site in decimal degrees, and the first and last dates of the sampling record for each site.

Site Name	LTM ID	State where site is located	Site latitude, decimal degrees	Site longitude, decimal degrees	First date sampled	Last date sampled
			MAINE LTM LAKES			
ANDERSON POND	1E1-131E	ME	44.6478	68.0597	21NOV82	19NOV88
LITTLE LONG POND	1E1-132E	ME	44.6375	68.0780	01MAY82	19NOV88
MUD POND	1E1-134E	ME	44.6330	68.0908	01MAY82	19NOV88
SALMON POND	1E1-135E	ME	44.6314	68.0861	01MAY82	19NOV88
TILDEN POND	1E1-133E	ME	44.6347	68.0722	01MAY82	19NOV88
			VERMONT LTM LAKES			
BIG MUD	1C1-100E	VT	43.3139	72.9305	10FEB82	24OCT89
BIG MUDDY	1C1-108E	VT	44.7556	72.6000	18FEB81	23OCT89
BOURN	1C1-089E	VT	43.1055	73.0028	17AUG82	25OCT89
BRANCH	1C1-101E	VT	43.0811	73.0186	30JAN81	25OCT89
COW MOUNTAIN	1C2-075E	VT	44.5611	71.7028	23FEB81	03OCT89
FORESTER	1C3-076E	VT	43.0817	72.8680	05MAR81	10OCT89
GRIFFITH	1C1-109E	VT	43.3022	72.9597	21JAN82	26OCT89
GROUT	1C1-090E	VT	43.0455	72.9458	20FEB80	11OCT89
HARDWOOD	1C1-091E	VT	44.4680	72.5000	28JAN82	19OCT89
HAYSTACK	1C1-110E	VT	42.9167	72.9167	20FEB80	07NOV89
HOWE	1C1-112E	VT	42.7856	72.9875	20F3B80	01NOV89
KETTLE	1C3-064E	VT	44.2944	72.3189	05FEB80	18OCT89
LILY	1C1-092E	VT	43.2342	72.7514	19FEB80	10OCT89
LITTLE, WINHALL CO.	1C1-094E	VT	43.1236	72.9417	21JAN82	08NOV89
LITTLE, WOODFORD CO.	1C1-093E	VT	42.9250	73.0653	20FEB80	02NOV89
LITTLE ROCK	1C1-104E	VT	43.400	72.9556	01JUL82	24OCT89
OSMORE	1C2-073E	VT	44.3083	72.2792	05FEB80	13OCT89
PIGEON	1C2-071E	VT	44.2458	72.3292	07FEB80	17OCT89
SOUTH, MARLBORO CO.	1C3-075E	VT	42.8439	72.7125	19FEB80	31OCT89
STAMFORD	1C1-095E	VT	42.8222	73.0653	27JAN82	01NOV89
STRATTON	1C1-096E	VT	43.1042	72.9694	20FEB80	08NOV89
SUCKER	1C1-106E	VT	42.8250	73.1292	05MAR81	02NOV89
SUNSET	1C1-097E	VT	42.9194	72.6833	19FEB80	31OCT89
UNKNOWN	1C1-098E	VT	44.9097	71.8444	21JUN82	04OCT89
			ADIRONDACK LTM LAKES			
ARBUTUS	1A1-052O	NY	43.9875	74.2417	19FEB83	26NOV89
BIG MOOSE LAKE	1A1-103O	NY	43.8292	74.8500	30JUN82	25NOV89
BLACK	1A1-071O	NY	44.4391	74.2939	30JUN82	25NOV89

(Continued)

Site Name	LTM ID	State where site is located	Site latitude, decimal degrees	Site longitude, decimal degrees	First date sampled	Last date sampled
		ADIRONDACK LTM LAKES (Continued)				
BUBB LAKE	1A1-113O	NY	43.7708	74.8542	30JUN82	25NOV89
CASCADE LAKE	1A1-105O	NY	43.7911	74.8041	30JUN82	25NOV89
CLEAR POND	1A2-077O	NY	44.000	73.8222	30JUN82	26NOV89
CONSTABLE	1A1-017O	NY	43.8333	74.7958	30JUN82	25NOV89
DART LAKE	1A1-106O	NY	43.7972	74.8583	30JUN82	25NOV89
HEART LAKE	1A1-102O	NY	44.1822	73.9694	30JUN82	25NOV89
LAKE RONDAXE	1A1-110O	NY	43.7639	74.9055	30JUN82	25NOV89
LITTLE ECHO POND	1A1-107E	NY	44.3055	74.3975	30JUN82	25NOV89
MOSS LAKE	1A1-109O	NY	43.7861	74.8500	30JUN82	25NOV89
OTTER LAKE	1A2-078O	NY	43.1880	74.5000	30JUN82	26NOV89
SQUASH POND	1A1-111O	NY	43.8264	74.8897	12DEC82	25NOV89
WEST POND	1A1-112O	NY	43.8111	74.8792	30JUN82	25NOV89
WINDFALL LAKE	1A1-087O	NY	43.8110	74.8500	30JUN82	25NOV89
		UPPER MIDWEST LTM LAKES				
ANDRUS	2B3-082E	MI	46.7000	85.0403	05NOV83	25OCT89
BASS	2B2-043E	MI	46.4639	85.7167	04NOV83	23OCT89
BUCKEYE	2B2-102E	MI	46.4658	85.7386	03NOV83	24OCT89
CAMP TWELVE	2C1-075E	WI	45.9482	89.3706	14NOV83	17OCT89
CLEAR	2C1-074E	WI	45.3667	89.2306	08NOV83	19OCT89
CRUISER	2A2-063E	MN	48.4983	92.8053	01NOV83	31OCT89
CUSINO	2B2-105E	MI	46.4544	86.2583	03NOV83	24OCT89
GREATER BASS	2C1-065E	WI	45.3569	89.1917	08NOV83	19OCT89
JOHNSON	2B1-047E	WI	46.4250	85.0439	05NOV83	25OCT89
KELLY	2B3-083E	MI	46.4400	85.6458	05NOV83	25OCT89
LAKE CLARA	2C2-058E	WI	45.5122	89.5708	08NOV83	16OCT89
LOCATOR	2A2-067E	MN	48.5405	93.0036	01NOV83	31OCT89
LOITEN	2A2-066E	MN	48.5258	92.9233	01NOV83	31OCT89
LONG (WI)	2C1-073E	WI	45.7167	89.6042	02MAY84	17OCT89
LUNA	2C2-062E	WI	45.9053	88.9597	01NOV83	18OCT89
MCGRATH	2C1-029E	WI	45.7917	89.6444	07NOV83	16OCT89
MCNEARNEY	2B1-048E	MI	46.4264	84.9583	04NOV83	23OCT89
MONOCLE	2B3-081E	MI	46.4750	84.6458	04NOV83	23OCT89
MORGAN	2D3-071E	WI	45.7742	88.5430	06NOV83	18OCT89
MURRAY	2B2-101E	MI	46.4708	85.7014	03NOV83	23OCT89
NEVINS	2B2-106E	MI	46.5167	86.2430	03NOV83	24OCT89

(Continued)

Site Name	LTM ID	State where site is located	Site latitude, decimal degrees	Site longitude, decimal degrees	First date sampled	Last date sampled
		UPPER MIDWEST LTM LAKES (Continued)				
NICHOLS	2C1069E	WI	46.1039	89.6875	07NOV83	17OCT89
SAND	2C1-068E	WI	45.7244	89.6514	07NOV83	16OCT89
SHOEPACK	2A2-065E	MN	48.5036	92.8833	01NOV83	31OCT89
STUART	2B2-103E	MI	46.5900	85.5097	04NOV83	23OCT89
SUGAR CAMP	2C2-063E	WI	45.8000	89.3042	08NOV83	19OCT89
SUNSET	2C1-063E	WI	45.9264	89.3375	08NOV83	19OCT89
VANDERCOOK	2C1-064E	WI	45.9819	89.6869	07NOV83	17OCT89
		COLORADO LTM LAKES				
BIG ELDORADO LAKE	4E2-066E	CO	37.7133	107.543	31JUL85	11SEP89
LAKE ELBERT	4E1-063E	CO	40.6341	106.707	18JUL85	06SEP89
LITTLE ELDORADO LAKE	4E2-067E	CO	37.7133	107.546	31JUL85	12SEP89
LONG LAKE RESERVOIR	4E2-068O	CO	40.4758	106.690	16JUL85	11OCT89
LOWER SUNLIGHT LAKE	4E2-069O	CO	37.6344	107.579	31JUL85	26AUG88
SEVEN LAKES	4E2-009E	CO	40.8955	106.681	15JUL85	08SEP89
SUMMIT LAKE	4E2-060O	CO	40.5458	106.680	16JUL85	11OCT89
UPPER GRIZZLY LAKE	4E3-065O	CO	37.6219	107.385	31JUL85	28JUL88
UPPER SUNLIGHT LAKE	4E2-070O	CO	37.6278	107.580	31JUL85	26AUG88
WHITE DOME LAKE	4E2-071O	CO	37.7089	107.553	31JUL85	12SEP89
		CATSKILL LTM STREAMS				
BEAVERKILL	01417820	NY	42.0172	74.5819	03NOV83	07DEC89
EAST BRANCH NEVERSINK, HEADWATER	0143400690	NY	41.9725	74.4485	13JUN84	26JUN89
EAST BRANCH NEVERSINK, MIDREACH	01434010	NY	41.9633	74.4553	15AUG83	08DEC89
HIGH FALLS BROOK	0143410505	NY	41.9758	74.5219	15AUG83	23JUN89
HOLLOW TREE BROOK	01362342	NY	41.1422	74.2653	21JAN85	05DEC89
ROUNDOUT CREEK	01364959	NY	41.9367	74.3764	16AUG83	02JAN90
WOODLAND CREEK	01362285	NY	42.0394	74.3336	15AUG83	05DEC89

APPENDIX B

PERIOD OF RECORD FOR THE VARIABLES IN EACH LTM REGION

The period of record for each variable is identified for each region in this appendix. The table was constructed by obtaining the first and last dates of the period of record for all sites within each region, thus each site within the region does not necessarily have data for the entire period identified. For definitions of the variables listed here, see Table 5-3.

LISTING OF THE CHEMICAL VARIABLES IN THE LAKE AND STREAM FILES AND THEIR PERIODS OF RECORD IN EACH LTM REGION

Variable	Maine	Adirondacks	Vermont	Upper Midwest	Colorado	Catskills
ALFIL	02APR83 14NOV89		25JAN83 08NOV89	01NOV83 31OCT89	15JUL85 12SEP89	15AUG83 13SEP89
ALMON		30JUN82 26NOV89				
ALORG		30JUN82 26NOV89				
ANC	01MAY82 14NOV89	30JUN82 26NOV89	27JAN81 08NOV89	01NOV83 31OCT89	15JUL85 11OCT89	15AUG83 02JAN90
CAFIL	01MAY82 14NOV89	30JUN82 26NOV89	05FEB80 08NOV89	01NOV83 31OCT89	15JUL85 11OCT89	15AUG83 08DEC89
CLFIL	01MAY82 14NOV89	30JUN82 26NOV89	12JUN80 08NOV89	01MAY84 31OCT89	15JUL85 11OCT89	15AUG83 02JAN90
COLTRU	07JUL83 14NOV89		05FEB80 08NOV89	01NOV83 31OCT89	15JUL86 12SEP89	
COND	27APR84 14NOV89	30JUN82 26NOV89	12JUN80 08NOV89	01NOV83 31OCT89	15JUL85 11OCT89	15AUG83 08DEC89
DIC		30JUN82 26NOV89			15JUL85 12SEP89	
DOC	08NOV85 14NOV89	30JUN82 26NOV89		01MAY84 31OCT89	15JUL85 12SEP89	15AUG83 29OCT89
FFIL		30JUN82 26NOV89		01NOV83 31OCT89	15JUL85 11OCT89	
FLOW						15AUG83 05DEC89
KFIL	01MAY82 14NOV89	30JUN82 26NOV89	13JUL82 08NOV89	15JUL85 31OCT89	15JUL85 11OCT89	15AUG83 08DEC89
MGFIL	01MAY82 14NOV89	30JUN82 26NOV89	05FEB80 08NOV89	01NOV83 31OCT89	15JUL85 11OCT89	15AUG83 08DEC89
NAFIL	01MAY82 14NOV89	30JUN82 26NOV89	13JUL82 08NOV89	15JUL85 31OCT89	15JUL85 11OCT89	15AUG83 08DEC89
NH4FIL		30JUN82 26NOV89		01NOV83 31OCT89	15JUL85 12SEP89	
NO3FIL	01MAY82 14NOV89	30JUN82 26NOV89	04JUN85 08NOV89	01MAY84 31OCT89	15JUL85 11OCT89	15AUG83 02JAN90
ORGION	08NOV85 14NOV89	30JUN82 26NOV89		01NOV83 31OCT89	15JUL85 12SEP89	15AUG83 29OCT89

(Continued)

LISTING OF THE CHEMICAL VARIABLES IN THE LAKE AND STREAM FILES AND THEIR PERIODS OF RECORD IN EACH LTM REGION (Continued)

Variable	Maine	Adirondacks	Vermont	Upper Midwest	Colorado	Catskills
PH	28APR86 14NOV89	30JUN82 26NOV89	05FEB80 08NOV89	01NOV83 31OCT89	15JUL85 11OCT89	15AUG83 08DEC89
SECCHI	01MAY82 14NOV89		06MAY82 08NOV89			
SIFIL					15JUL85 11OCT89	
SIO2	27APR84 14NOV89	30JUN82 26NOV89		01NOV83 31OCT89		15AUG83 08DEC89
SO4FIL	01MAY82 14NOV89	30JUN82 26NOV89	12JUN80 08NOV89	01NOV83 31OCT89	15JUL85 11OCT89	15AUG83 02JAN90
STAGE		29JUL82 26NOV89				
WTEMP	01MAY82 14NOV89	30JUN82 26NOV89	05MAR81 08NOV89		15JUL85 11OCT89	